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PROCEEDINGS OF THE INTERNATIONAL COURSE

CERAMIC MATERIALS IN BUILDING HERITAGE:

CONSERVATION PROBLEMS AND INTERVENTION

Coordinated and co-organized by:
Youth in the Conservation of Cultural Heritage- YOCOCU España

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CERAMIC MATERIALS IN BUILDING HERITAGE:

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that took place in Madrid the 29th and the 30th of June, 2016 at the Instituto de Cerámica y Vidrio (ICV-CSIC), Madrid (Spain).

Coordinated and co-organized by: YOCOCU yOuth in COnservation of CUltural Heritage ESPAÑA

Co-organized by: IGEO Instituto de Geociencias; Instituto de Cerámica y Vidrio CSIC; Programa GeoMateriales Heritage Conservation

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INDEX

Ceramic material is a key element in the cultural heritage. We are indeed surrounded by ceramic elements as part of historic buildings, as well as archaeological and underwater ensembles, being used widely as both structural and/or decorative elements.

In the field of conservation and restoration, brick masonry has always received special attention due to its strong presence in the built heritage. Many other ceramic elements are part of this heritage, such as roofing tiles, pavements, or decorative techniques like wall tiling or the *trencadis*.

Ceramic material applied to architecture brings about specific problems when dealing with preservation and restoration interventions, being usually more prone to decay than other geomaterials. Different conservation issues arise when it comes to mixed structures, were different materials are used, leading to particularly complex scenarios from the conservation perspective. In these cases, the degradation process is directly related to the manufacture technologies, the environmental context and the general pathology of the building.

This course will provide a didactic overview of the problems related to the conservation of ceramic material in different contexts. It will follow a thematic evolution, from the selection of raw materials, to the influence of the context and main decay agents, to major intervention techniques and preventive conservation.

Knowledge about the origin and selection of suitable raw materials and better understanding of the technology used for the manufacture of ceramic elements involves important implications for the conservation of these materials. In this sense, it is also important to address characterization techniques for analysis and diagnosis, paying special attention to portable and non-destructive techniques. A correct analysis is essential when assessing the most appropriate intervention. Treatments such as desalination, consolidation or protection are reviewed and analysed. Further, a critical assessment of excessive interventionism will be addressed, since in some cases, this has resulted in the source of further damage. It is therefor key to emphasize the special importance of preventive conservation, a particularly complex matter when it comes to outdoor environment.

Finally, this thematic progression will be closed with the analysis of some case studies where subjects previously seen are illustrated.

For this purpose some of the most recognized professionals in the field are gathered in Madrid in June 2016, bringing closer this area of conservation to an international audience, students and professionals, and making it more visible to the general public.

Natalia Pérez Ema
President of YOCOCU España

TOPIC 1

Ceramic materials in building heritage: raw materials and processing

CERAMIC CONSTRUCTION MATERIALS IN CULTURAL HERITAGE: TYPOLOGIES, MANUFACTURE AND PROPERTIES

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1. Introduction

Ceramic materials have been widely utilized for the realization and decoration of buildings, at all times and in all places, up to today [1,2]. Their use was and is particularly common in areas that have scarce availability of suitable natural stone, while large quantities of clay are present, which are suitable for the production of structural and decorative ceramic material (artificial stone). For example, in Italy ceramic artifacts have been widely used in the Po valley, which is rich of clays, both of marine and continental origin [3].

The construction ceramic materials can have different functions and are used in different environments and climates, so that they are constituted by artifacts with appropriated characteristics. As a matter of fact, there are several kinds of artifacts (table 1); it deals mainly with structural artifacts, but also the decorative ones are very diffuse. Along with the real ceramic materials, it is opportune to take into consideration also the unfired bricks, which were largely used in the past, and also today, especially in areas with a hot and dry climate of the Earth [4, 5] Ultimately, processing technology and properties of the ceramic artifacts can vary and the personnel employed in conservation activities cannot avoid to know how they were manufactured and which are their properties.

2. Processing technology

All the ceramic products have the same general processing scheme: 1) raw material selection, 2) shaping, 3) drying, 4) firing, even though each type of product is characterized by some specific technology for the realization of each processing step [6-8].

Table 1. Ceramic artifacts used for the realization of architectonic structures.

STRUCTURAL	DECORATIVE
Bricks	Architectural terracotta
(Unfired bricks)	Glazed tiles
Roofing tiles	(Porcelain articles)

2.1 Raw materials

Clay is the unique raw material suitable for the production of ceramic materials, even though some additive can be introduced in order to slightly modify their workability or the properties of the finished product [3]. Clays are made of fine particles that can be kept together by adding water, thank to the presence of generally more than 50% of clay minerals. The mineral assemblage of the ceramic clays includes illite, kaolinite, quartz, feldspars and carbonates, with chlorite and smectite in less amounts. Other than the mineralogical assemblage, the ceramic clays are mainly characterized by chemical composition and grain size

distribution. Plasticity is their main technological property, that is the capacity to give, mixed with water, a consistent mass to which you can give a shape without breaking it.

Generally, the additives are substances that decreases the plasticity, so reducing the quantity of water during the shaping step, and making the drying phase easier. Common additives are sand and organic substances (such as straw and vegetable seeds), which burn during firing.

2.2 Manufacture

All ceramic materials were shaped at plastic state, by mixing clay with water (approximately 70/30) and eventually up to 30% of additive [6, 8, 9]. Hand making is the older shaping technology; the use of a mold, initially of wood and more recently gypsum, is also very ancient.

After shaping, the water-rich articles undergo the long and difficult drying phase, during which a big volume of water must be eliminated through slow evaporation at open air without provoking deformations and cracks.

The last step is the firing of the dried artifacts. At the beginning, firing was made preparing heaps of dried bricks mixed with wood, to which fire was then set. This firing system was characterized by different temperature and atmosphere in the various zones of the heaps, so that the finished products showed variable characteristics, even in different points of a single artifact. Best results were obtained, since the Roman period, with the use of especially developed furnaces (image 1), [10].

Image 1. Late Medieval ceramic furnace in the Po valley near Piacenza (Italy).

As for architectural terracotta, in some cases it has been ascertained that decorative motifs had been obtained by carving after firing [11].

More complex is the case of glazed tiles, largely utilized for flooring, wall coating and as roof coating of the dome of churches [12]. These articles undergo two additional production phases that are the application of a glaze layer, usually after the first firing, and the firing of the glaze. In case of application of a slip layer, it is normally applied on the surface of the dried piece, so that only one firing is necessary.

3. Properties of the finished products

From the conservation point of view, the most important properties of the construction ceramics are: color, porosimetric characteristics (open porosity and mean pore size), and mechanical resistance (table 2).

3.1 Color

The color of the ceramic artifacts can vary greatly from red to light red, from yellow to gray, depending on several conditions. The higher the iron percentage more intense is the color: red with oxidant firing atmosphere, gray with reducing atmosphere. The carbonate content in the clay tends to lighten the intensity of the color. The firing temperature has less influence.

Table 2. Main properties of ceramic products from the conservation point of view.

Characteristics	Measuring system	Frequent values	Observations
Color	Munsell tables	Red to light red; yellow to grey	The color depends on the iron percentage, the firing conditions and the carbonate content in the clay
Porosimetric characteristics			
Open porosity (% by volume)	Water absorption	15 - 30	Carbonatic clays give the highest values of open porosity, and vice-versa
	Mercury intrusion	25 - 40	
Mean pore diameter (μm)	Mercury intrusion	0.3 - 2	The mean pore diameter tends to increase when mean grain size of the clay and/or firing temperature increase
Mechanical properties			
Modulus of rupture ($kg \cdot cm^{-2}$)	Compression strength	300 - 350	Mechanical resistance decreases by increasing open porosity and increases with firing temperature
	Bending strength	70 - 110	

3.2 Porosimetric characteristics

Open porosity of ceramic construction materials is very high, but the results depend on the measuring method. If you use the method based on the amount of absorbed water, you will find values prevalently from 15 to 30 % by volume. The same products will show porosity from 25 to 40 % by volume with mercury intrusion porosimeter, due to the capacity of mercury under pressure to penetrate into smaller pores. In parity of other conditions, the content of carbonates in the clay increases the porosity. The pore size mainly depends on the grain size distribution of the clay: the higher the mean grain size larger are the pores. In addition, the mean pore size increases with increasing firing temperature.

3.3 Mechanical properties

The most important mechanical property to be considered should be the compression strength (CS), which is complicated to measure. Therefore, the bending strength (BS) is usually taken into account, considering that there is a quite good correlation between the two types of mechanical resistance: CS ≈ 3.7 BS [13, 14]. Mechanical resistance decreases as porosity increases, while generally it increases with firing temperature.

4. Degradation causes

The main degradation causes of ceramic artifacts used for external structures, in presence of water, can be individuated in the occurrence of freezing/thaw cycles and efflorescence. Both processes are controlled by the porosimetric characteristics [15- 17].

There is no freezing/thaw problem with the pores less than 0.1 μm approximately, where water cannot enter, and for those larger than 2 μm approximately. In general, the most dangerous pores are those with dimensions of 0.1-1 μm in diameter.

Efflorescence is a deposit of salts formed from water solutions on the surface of structures when water evaporates, therefore the formation of efflorescence mainly depends on the disposal of salts, which generally come from the soil. Water can flow inside the structure by capillary rise up to a height usually not more than three meters approximately. Other degradation causes, like anthropogenic factors and the wind, are much less important.

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TOPIC 2

Decay, degradation factors and mechanisms

UNDERSTANDING THE DETERIORATION OF OLD CLAY BRICKS

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1. Introduction

Old clay bricks belonging to historical buildings that have survived to date have suffered along centuries from deterioration and damage caused by climate, loading and occupational use. Therefore, the materials that we have to work with are weathered materials and not the original ones. The deterioration exhibited by old clay bricks is diverse and is mostly due to external environmental factors and to material and manufacture procedures. Although damage is essentially due to building design and construction, it can cause further deterioration or foster the deterioration of clay brick units.

Although deterioration of clay brick material from historic buildings is an inevitable phenomenon and, according to [1], one of the most widespread causes of deterioration is the lack of maintenance, it has been accelerated by pollution in the last decades.

In this paper, the main deterioration mechanisms will be analysed as well as the principal types of deterioration that occur in old clay bricks.

2. Deterioration mechanisms

The most important factors influencing deterioration of old clay bricks are mostly related to environmental action, raw materials and manufacture process, although the design and construction of the building, i.e. its shape, orientation and above all the details, may strongly influence the occurrence and severity of deterioration in clay bricks.

Environmental factors include for example the presence of moisture and soluble salts, air pollution, erosion from the wind, temperature changes, excessive loads and soil settlements, as well as attacks by biological agents. It must be noted that a large part of the degradation processes only occurs in the presence of water, consequently, the speed at which a material absorbs and releases water has a strong influence on its risk of degradation. Therefore, moisture transport properties (porosity and pore size distribution) are of primary importance when considering the durability of clay brick. Thus, the way moisture affects old clay bricks is highly dependent on the raw materials used and the manufacturing process.

Table 1 presents an overview of the most important damage processes affecting clay brick and the damage types related to those processes. This article will focus on how deterioration occurs and what are the main causes of deterioration in old clay bricks.

Table 1. Overview of the principal deterioration processes and related deterioration types

Damage processes		Most important damage types
Physical / chemical	Moisture; Salts; Frost; Pollution; Biological organisms	Biological growth; Efflorescence; Spalling; Exfoliation; Powdering; (Black) crust
Structural	Overloading, creep	Crack patterns

3. Moisture

Water is one of the most important agents of deterioration of old clay bricks since, primarily, it is a vehicle of transport for harmful substances (atmospheric contaminants, in particular CO_2, soluble salts, living organisms). In old buildings, damages associated with the capillary rising water are usually more severe than those caused by the rain [2].

Water can infiltrate and progress inside clay bricks by capillarity ascension from weak points of the structure (defective mortar joints, cracks, open pores), being direct rain exposure, defective drainage systems and the underground water table the main sources of moisture. The damage can arise from the formation of destructive salt crystals and from freezing/thawing cycles in countries with sub-zero temperatures.

Salts may be originally present in the material (e.g., clay bricks made using seawater or using uncleaned/untreated clays), they may come from the environment (aerosols, de-icing salts) or from the use of the building in the past (e.g., chloride from salt storage and kitchens, nitrates in the case of stables). The presence of these salts, combined with the high porosity of old clay bricks, can give rise to the formation of salt crystals. Generally, the formation of soluble salt crystals exposes the material to considerable stresses in the pore walls, which results in the premature deterioration of the brick. Old clay bricks contain, typically, calcium (Ca^{2+}), sodium (Na^{+}), potassium (K^{+}), magnesium and iron sulfates that come from impurities and the constituents of raw clay, water and from lime mortars, while the contamination by chlorides and nitrates comes generally from the subsoil [3].

Under adequate temperature and relative-humidity conditions, these salts are dissolved in contact with water and crystallize. The crystallization of these salts within the pores leads to a high volume increase and to states of high stresses, called crypto-efflorescence. The pressure developed within the pores can exceed the mechanical strength of the material and, subsequently, cause the disintegration of the superficial layer of the clay bricks [3], [4]. Due to water migration and evaporation, these salts are also transported towards the external surface of bricks where they crystalize producing efflorescence [5]. The manifestation of efflorescence is related with the amount of soluble salts present in the original raw clay. The higher is the percentage of soluble salts, the greater will be the probability of the clay brick to exhibit efflorescence. As a consequence of salt crystallization, old clay bricks may show deterioration like powdering, exfoliation and spalling.

Moreover, the crystallization of soluble salts is influenced by the porosity of the brick (open or closed porosity), the capacity of water absorption (at least an absorption of 6 % is necessary to produce the phenomena of efflorescence), the crystallization mechanism and water evaporation [2].

According to several authors [5], [6], [7], [8], the most frequent and more damaging salts are sulfates (e.g., sodium sulfate Na_2SO_4), nitrates (e.g., sodium nitrate $NaNO_3$) and chlorides (e.g., sodium chloride NaCl,). These salts are generally present in ratios of 0.5 to 3.5 % of the dry weight of the brick, reaching, exceptionally, values up to 5-7 %. In [9] were described clay bricks from the Byzantine period that evidenced signs of efflorescence with the following types of salts: chlorides (20 %), nitrates (36 %) and sulfates (44 %). Certain bricks were splintered, broken or even reduced to dust due to the destructive action of these salts.

When soluble salts are present in low proportions, clay bricks are not always sensitive to this phenomenon. Bricks from the 16th century exhibiting low ratios of aggressive salts where efflorescence was not observed were described in [10]. Similarly, old clay bricks that contained salts (nitrate and sulfate) in low and harmless concentrations were found in [11].

Furthermore, as clay bricks and mortar (e.g. bedding mortar, plaster) are used in combination with each other, the risk and location of salt damage will depend on the pore size distribution of the two materials [12]. Since moisture (and salt) transport by capillarity moves from larger to smaller pores, a fine porous clay brick in contact with a coarse porous mortar will have a larger risk of decaying than a coarse brick applied on a fine porous mortar.

Water is a serious concern in countries where negative temperatures occur frequently. When the water present in the pores of bricks freezes, the crystals exert a high pressure on the internal structure of the material, causing usually its fracture or disintegration [3]. The susceptibility of the clay bricks to the freezing water is essentially related with the size and distribution of its internal pore structure. Generally, the resistance of old clay bricks to the freezing water depends essentially on the way water penetrates and stays within the pore structure of the material. Very porous bricks with a large percentage of open pores have a low resistance to the action of ice, as water easily penetrates within the pores. Additionally, for the water to freeze, it is necessary that pores have enough space for the ice crystals to form [3], which means that bricks with large pore sizes are more susceptible to frost damage than bricks with a thin pore size. On the other hand, it was observed in [7] that the existence of pores with diameter higher than 3 μm is beneficial for the resistance to the freezing water, while smaller pores are prejudicial, due to the higher volume of freeze water it can tolerate. This agrees with [2], where it was found that clay bricks burned at low temperature, like the majority of historical clay bricks, are more vulnerable to the action of freezing water because they contain an important percentage of fine and open pores. Thus, the bricks with high percentage of very fine pores (between 0.25 and 1 μm) have also a lower durability due to freezing action. According to [13] and [14], fissures and small dimension pores (< 1 μm) are further promoted by carbonates during the firing process.

4. Temperature

Daily and seasonal changes of air temperature, causing expansion and contraction cycles of clay bricks, may give rise to degradation phenomena in masonry due to differential thermal dilation and can create new cracks or increase already existing ones. Cracks usually increase the deterioration rate of the materials, allowing the penetration of water and aggressive agents.

Extreme temperatures as those produced by fire can have catastrophic effects. If the bricks have been burned at higher temperatures than those that normally take place during fires, these bricks provide, generally, good resistance to fire. In a more severe fire, the occurrence of cracking and large deformations due to the clay brick thermal expansion are expected together with spalling on the exposed surfaces.

Reddish clay bricks are produced at temperatures around 800 to 1100ºC. Therefore, it is expected that many old clay bricks have been fired around this temperature, as this colour is the most common. Although the average temperature of a fire is around 550ºC, the variability of the material and the deficiencies during the production process, it is possible that many old clay bricks have not developed enough fire resistance during the firing process.

5. Biological deterioration

The deterioration by biological agents is not an isolated phenomenon but the result of the interaction of numerous factors [15]. Seaweeds, lichens, mosses and vegetation produce physical and chemical damage. Some examples are the fracture, disintegration and the attack by organic and inorganic acids produced by micro-organisms and vegetation.

Biological deterioration can also be caused by soil deposits that contain humus and insects. The mechanical action of the roots, especially of large plants and trees, can also produce important cracks. The acid contained in the excrements of birds and animals, particularly of the pigeons, is corrosive and can produce chemical damage in the bricks. In addition, the excrements can be also a source of bacteria and can act as a fertilizer for the vegetation.

6. Air pollution

Modern societies produce large amounts of prejudicial particles for old clay bricks from diverse origins, such as the emissions of industrial parks (cement or paper industries, chemical plants), domestic and industrial air conditioner and heating systems, and the emissions from vehicles. Frequent contaminants are the sulphur dioxide (SO_2) and the carbon dioxide (CO_2). SO_2 reacts with the oxygen of air and the water in the pores of bricks to produce sulfuric acid (H_2SO_4). The reaction of this acid with clay bricks helps the formation and crystallization of salt compounds. For example, the reaction of H_2SO_4 with Ca^{2+}, Na^+ and K^+ produces the soluble salts $CaSO_4$, Na_2SO_4 and K_2SO_4, with all the consequences described earlier [16].

The reaction of moisture with lime compounds found in bricks, and in lime based mortars, can originate the creation of lime nodules that can lead to an increase of the internal stresses, resulting in cracking and delamination [17].

Other pollutants present in the atmosphere due to industrial pollution can also react with the brick's clayey constituents. With the water from rainfalls, hydrochloric and nitric acids are produced, and responsible for important alterations in the siliceous constituents of clay bricks.

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BIOLOGICAL COLONIZATION AND BIODETERIORATION OF ARCHITECTURAL CERAMIC MATERIALS

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The impact of microbial activity on the deterioration of cultural heritage is a well-recognized global problem. Architectural ceramics constitute an important part of the worldwide cultural heritage. When exposed outdoors, biological colonization and consequently biodeterioration may occur. A vast biodiversity has been identified on ceramic materials, from bacteria to more complex organisms, such as plants. This worldwide problem can cause functional, physical and chemical damages on most of the architectural ceramic materials.

1. Introduction

Architectural ceramics as building materials are used in the construction and ornamentation of architectural work. Buildings and monuments with ceramic elements can be found throughout the world. This work describes the biological colonization and biodeterioration of architectural ceramics, namely bricks and architectural sculptures, roofing tiles and glazed wall tiles, focusing only on traditional ceramics (clay-based) described in the literature review by Coutinho et al [1].

2. Biodeterioration

The deterioration of ceramic materials, as in other building materials, is influenced by the characteristics of the substrate (e.g. mineralogical composition, porosity and surface roughness), environmental agents (e.g. wind, sunlight, temperature, rain and relative humidity), microclimatic conditions (e.g. local urban geometry, building design or adjacent materials), atmospheric pollution and biological colonization. Living organisms are capable of interacting with materials causing changes in their properties. Whenever these changes are undesirable they are referred to as biodeterioration (Hueck 1965). Image 1 presents examples of biodeterioration on different architectural ceramic.

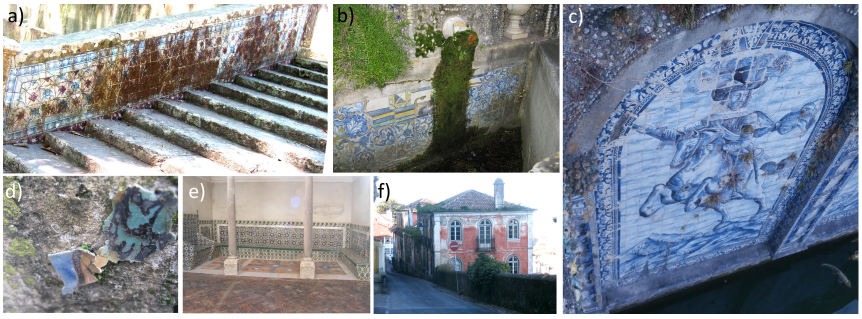

Image 1. Examples of biodeterioration on different architectural ceramic materials: (a) North-facing tile panel from Casa da Pesca covered with a brown biofilm, (b) Tiles from a fountain located in Fronteira Palace with phototrophic microorganisms, mosses and vascular plants, (c) Tiles from the Fronteira Palace with vascular plants in the mortars, (d) glaze detachment due to growth of bryophyta in the Fronteira Palace, (e) ceramic floor tiles with dark coloured biofilm and (f) ceramic roofing tiles with dark biofiom and vascular plants colonization.

In the case of ceramic cultural heritage assets, biodeterioration can be functional, physical and chemical (Table 1), and most of the times, these three deterioration forms intertwined. Table 1 summarizes the most common forms of deterioration described in the literature.

Table 1. Summary of the most common forms of ceramic biodeterioration.

	Cause	Damages
Functional Biodeterioration	• production of organic pigments and development of colored biofilms on surfaces	• change of the visual appearance of the materials [2-5]
	• development of biofilms and accumulation of microbial biomass	• alteration of isolation (thermal and hydric) and solar reflectance [6-7]
Physical Biodeterioration	• volume changes of microbial cells during growth • penetration of biological structures • extracellular polymeric substances (EPS)	• disintegration of the ceramic matrix and spalling of glazes [4][8-10]
Chemical Biodeterioration	• direct action of metabolic products exuded by organisms	• increase of capillary porosity of the ceramic body [2][11-13] • lixiviation [14] • chemical alteration [15] • efflorescences [17-16]

3. Microorganisms on architectural ceramic materials

Biological colonization is strongly dependent on environmental conditions (e.g. wind, sunlight, temperature, rain, relative humidity), microclimatic conditions and atmospheric pollution [18](Warscheid and Braams, 2000), with even the least bioreceptive surfaces being readily colonized. The role and typology of the architectural ceramic materials determine their exposure to weathering factors and consequently to biological colonization.

The overall biodiversity of ceramic materials described in the literature from 1972 to 2014, reported a total of 70 bacterial taxa, 97 cyanobacteria, 65 algae, 49 fungi, 9 lichens, 4 mosses and 18 vascular plants identified as ceramic-dwelling organisms [1]. Image 2 shows diverse types of microorganisms on ceramic and glazed substrates. The identification of microorganisms was mainly performed by culturing methods, except for bacteria which were

mostly identified by DNA-based analysis. Lichens, bryophytes and vascular plants were identified by phenotypic identification. At the current state of knowledge it was not possible to establish any relation between a given organism and a certain ceramic typology.

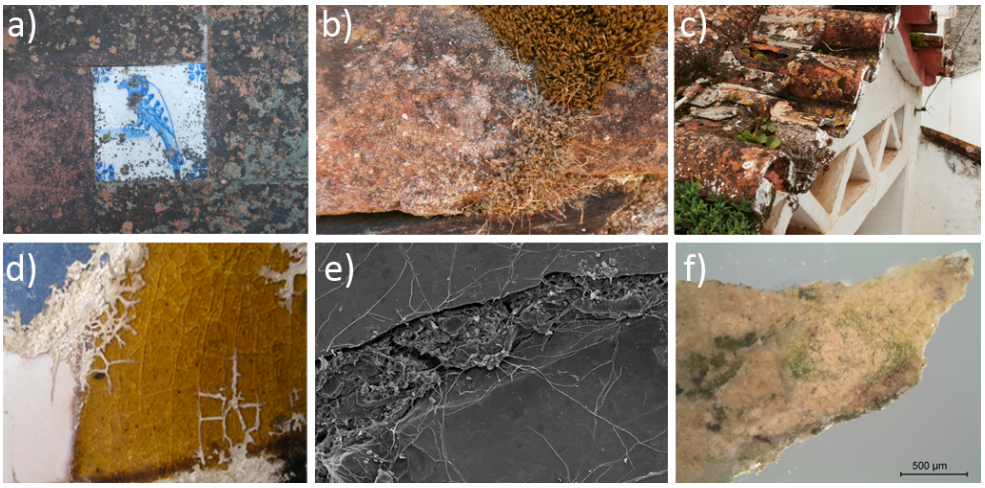

Image 2. Microorganisms on architectural ceramic materials: (a) biological colonization by lichens of the unglazed and glazed ceramic elements of a garden bench situated in Sintra (Portugal),(b) mosses colonizing Roman bricks of Ammaia (Portugal), (c) lichens and vascular plants colonizing ceramic roofing tiles, (d) glazed wall tiles from the Sintra National Palace (Portugal) colonized by lichens, (e) SEM image of biological biofilm in a glaze fracture in the tiles from Pena National Palace (Portugal) and (f) Optical microscopy image of ceramic-glaze interface colonized by phototrophic microorganisms.

4. Bioreceptivity of architectural ceramic materials

The susceptibility of a given material to biological colonization is based on its intrinsic properties and was defined by Guillite [19] as bioreceptivity. In the case of ceramic materials the relation between intrinsic properties and bioreceptivity has been appraised by different researchers through laboratory-based colonization experiments (e.g. [20-26]). Ceramic bioreceptivity is mainly associated with ceramic physical characteristics, such as porosity and surface roughness. Thus, the conservation condition of the materials is an important factor in bioreceptivity [9]. Similar to other inorganic materials a weak relationship between chemical composition and bioreceptivity has been established [20-21]. However, the pH was been pointed out as a factor causing inhibition of microbial growth on ceramic substrates [26].

5. Investigation and control of biodeterioration

Currently, the main issues to be investigated in the area of biodeterioration of inorganic building materials, that are part of our cultural heritage, can be summarized as (i) characterization of biological community and its interaction with the substrate which is usually based on taxonomic identification of colonizing organisms and analysis of the colonized substrate; (ii) laboratory experiments to investigate the bioreceptivity and biodeterioration, in order to overcome the complexity of deterioration factors and be able to understand biodeterioration mechanisms; and (iii) research on control of microorganisms and preservation methods to draw effective conservation strategies.

The eradication of microorganisms from inorganic building materials can be achieved by several methods often combining more than one procedure [27-29], such as mechanical methods, physical methods (radiation ultra-violet light, gamma-radiation, microwaves, thermal-treatment) or chemical methods [29].

In conclusion, biodeterioration of ceramic building materials causes cultural and economic problems, since it seriously affects the properties, functionality, durability and resistance of the materials. Thus, further research is crucial for understanding ceramic biodeterioration mechanisms and carry out accurate and effective conservation interventions.

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BRICKS AND CERAMICS IN UNDERWATER ENVIRONMENT: CHARACTERIZATION AND DEGRADATION

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1. Introduction

In the last decades, the archaeological research carried out with scientific methods has extended its field of action to the underwater heritage, through the experimentation of new techniques aiming to the conservation of submerged artifacts. The decay of underwater materials is a process that develops through physical and chemical events, such as biological colonization by microorganism, ionic corrosion and oxidation, which, sometimes, can cause serious alterations. The deterioration of both natural and artificial stone materials will depend on several factors associated to their intrinsic properties such as composition, porosity, water absorption, hardness and strength, as well as to environmental conditions to which they are exposed. The biodeterioration of structures immersed in seawater is a phenomenon that compromises the integrity of materials and is mainly caused by marine borers and fouling organisms. In particular, submerged stone materials are subject to bioerosion since they can provide a suitable substrate for the growth of many organisms. Marine biofouling can be divided in two main categories, macro and micro. Macrofouling is composed of sea weeds and macroscopic animals including barnacles, mussels, bryozoans and serpulids, whereas microfouling refers to different microorganisms such as bacteria and fungi .This lecture represents a contribution to the diagnostic study of marine archaeological bricks. In particular it is focused on the results related to two funded research project in the field of diagnostic and conservation of underwater cultural heritage: a) “COMAS” (Planned COnservation, *in situ*, of underwater archaeological artifacts), b) Innovative approaches applied to the experimental study of underwater ceramics, both funded by the Italian Ministry of Education, Universities and Research (MIUR).

2. Experimental setting

About fifteen brick specimens were collected from the “*Villa a Protiro*” area, in the submerged archaeological park of Baia, (Naples, Italy). This area was chosen for its large variety of architectural structures. Analytical procedures used were addressed to characterizing both the materials, and the degradation products, mainly bio colonization. In particular, microscopic observations on thin and stratigraphic sections were performed in order to define the textural characteristics of samples and the extent of their decay. The mineralogical characterization was carried out by X-ray powder diffraction analysis (XRPD), with the aim of identifying the constituent phases and to roughly estimate the firing temperature of bricks. The study of degradation products and identification of the biological species colonizing the samples were carried out through observations under a stereomicroscope and a scanning electron microscope equipped with EDS. Identification of mineralogical phases constituting the superficial deposits and concretions was obtained through Fourier transform infrared spectroscopy.

In order to deeper understand the relationship between brick properties and its susceptibility to biodegradation, it has been carried out an innovative experimental approach, specifically designed for appraising any compositional alteration originated after the protracted contact between ceramic and seawater. The experimental methodology consisted

of the manufacture of ceramic test-pieces with compositional and textural characteristics generally showed by underwater archaeological bricks. In particular, Experimental ceramic pastes were produced using different clays and sands with individual mixing and tempering procedures. Specifically, a "calcareous clay" (CaO > 5% wt) or a "non-calcareous" clay (CaO < 5% wt) were mixed with volcanic or sedimentary sands, even using various relative proportions of temper. Raw materials were previously characterized in terms of mineralogical and chemical composition by using, respectively, X-ray powder diffraction (XRPD) and X-ray fluorescence spectrometry (XRF). The ceramic test-pieces, carefully analysed by XRF after firing at 800 and 950 °C under oxidizing conditions, were successively placed into different underwater environments both natural and laboratory-simulated.

3. Results and discussion

The microscopic analysis of bricks taken from Baia, performed following the descriptive scheme proposed by Whitbread, allowed to recognize two different paste types. Specifically, the first type is medium-coarse grained and characterized by a microstructure with predominant vughs (macrovoids), and subordinate vesicles and linear voids. The groundmass is mainly homogeneous, its color in PPL varies from being light brown to dark brown, rarely reddish-brown. The optical activity is medium. Amorphous concentration features (Acf), mainly given by pure nodules with size comprised between 0.3 and 2 mm and impregnant portions, can be frequently observed. Inclusions, sub-rounded to angular, display a moderately homogeneous distribution in almost all examined bricks. They mainly consist of monocrystalline quartz, feldspar, muscovite, biotite, amphibole, clinopyroxene, iron oxides and rare chamotte. Fragments of volcanic rocks were also observed. The second type is fine grained and characterized by a microstructure with vughs (macrovoids) and vesicles with a smooth surface.

In some cases, voids show a preferred orientation parallel to the sample's margins. The groundmass is mainly homogeneous, its color in PPL is light brown to dark brown. Inclusions, sub-rounded to angular, mainly consist of quartz and plagioclase. All samples show the development of deposits shows different characteristics in the two above described pastes. The first type, constituted by coarse volcanic temper, shows thinner superficial layers. Conversely, the fine paste, mainly consisting of quartz temper, is characterized by superficial patinas with a greater thickness (about 0.5 mm). Morphological investigations allowed the identification of biological taxa that led to the degradation of substrates. Specifically, bricks show, in large amounts, diatoms and endolithic algae (both belonging to marine fitobenthos), along with spicules, probably referring to epilithic sponges (zoobenthos): they are stick-shaped with both pointed ends and with a calcitic composition. Macroalgae (mainly *Rhodophyceae*), whose encrustations are compact and flattened and cover the stone surface, serpulids (Anellida, Sedentaria) and Bryozoans (fouling organisms which play a "bioprotective" role on colonized samples, even if leading to an "aesthetic" alteration). The main organisms responsible for biodeterioration are encrusting species, such as serpulids and bryozoans, that colonize the surface generating a calcareous de- posits whitish in color, leading to an "aesthetic" alteration of the stone substrate. Furthermore, a larger amount of algae was identified in bricks.

In addition, physical degradation phenomena in bricks depend on the composition of raw material used, more precisely: the temper. Indeed, results highlighted that the paste with volcanic temper shows a greater resistance to biological colonization than that with quartz temper. The mineralogical composition of patinas was obtained through FT-IR analysis, which confirmed the carbonate nature of encrustations.

Regarding the experimental research carried out on laboratory made samples, the study confirmed that the type of raw materials (both raw clays and temper), as well as the different temper packing and firing temperatures are all key factors affecting porosity, kinetics of capillary water absorption and, consequently, the durability of a ceramic artifact. In particular, the different behavior of a ceramic paste to capillary water absorption and salt crystallization processes is related to specific pore size distributions and the development of a secondary open porosity after firing. Specifically, between the two different series of ceramic pastes experimentally produced (one with non-calcareous clay and volcanic temper and the other one with calcareous clay and silico-calcareous temper), the second displays a greater water absorption and a major susceptibility to salt crystallization phenomenon which, as is known, represents a main risk for conservation purposes. Therefore, the obtained data suggest that a deep knowledge of the intrinsic characteristics of a ceramic find recovered from underwater excavations is needed in the restoration field, in order to optimize the choice of the most suitable restoration procedures before musealization. The use and effectiveness of specific treatments are, in fact, essential to the future conservation of ceramics artifacts.

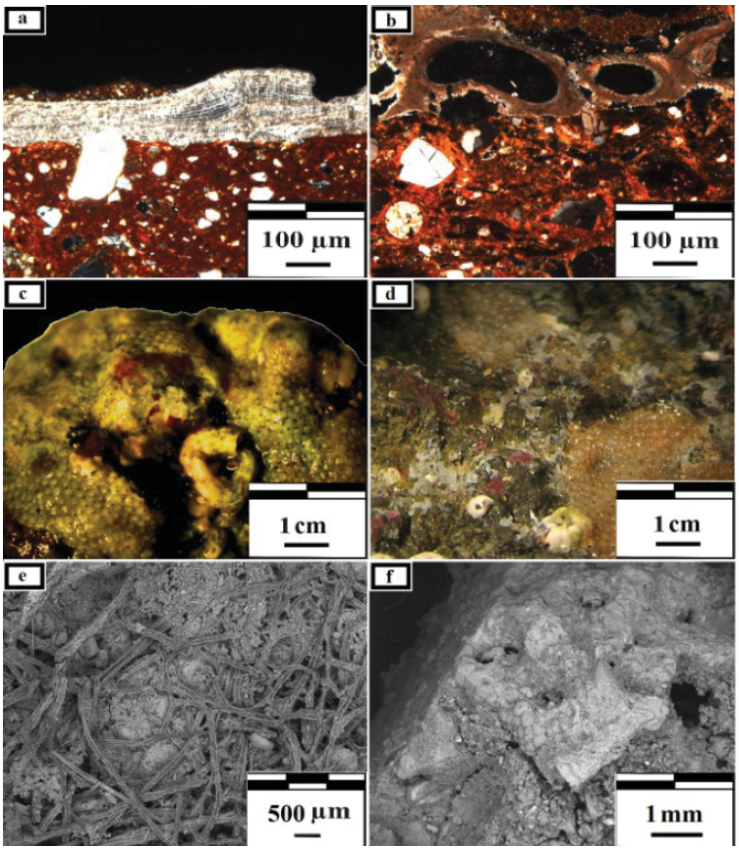

Image 1. Photomicrographs of superficial deposits on bricks fragments by using: POM (a, b); stereomicroscope (c, d) and SEM (e, f).

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TOPIC 3

Analytical techniques for characterization and conservation studies

ARCHAEOMETRIC CHARACTERIZATION OF HISTORICAL CERAMIC MATERIALS: BRICKS, ROOFS, AND DECORATIVE TILES

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Ceramic materials have been used by the human being from more than 10.000 years ago. In fact, ceramics are the first synthetic material, the most ancient artificial material created by prehistoric communities. Apart from recipients and containers, ceramic materials were promply used in building structures. Firstly as wall plasters and sun dried bricks, and later in time as fired bricks, roofs, and glazed tiles.

Current research on ceramic materials in building heritage has an increasing demand for new methodologies to extract as much technological and historical information as possible on these materials. Such kind of information cannot be extracted by using only traditional methods but also by using a combined approach with archaeometric characterization techniques. Among the topics demanded to archaeometric techniques are technology and processes of production, raw materials characteristics and provenance, as well as the current state of conservation and future preservation. Some of these topics are of key relevance, for instance, in certain conservational practices of monumental buildings which tend to use ancient or traditional style roof tiles and bricks in restoration and conservation tasks.

Most of the instrumental characterization techniques used in archaeometric approaches comes from the Materials Science discipline and concerns with the systematic study of composition, structure, and technological parameters of ceramics and their raw materials. On the whole, the archaeometric techniques for ceramic materials, which should be used in conjunction with historical and architectural data, are classified into direct or non-direct observation or analytical techniques. In the first case, they are not destructive and, consequently, a sample of the material is not needed. In the second case, the techniques are destructive or micro-destructive and a sample of the material needs to be necessarily taken. Among non-direct techniques are those which determine the mineralogical composition of a ceramic material, such as petrographic microscopy through thin section and X-ray diffraction (XRD), and their microstructural features, such as scanning electron microscopy (SEM); whereas other techniques yield some complementary information on thermal evolution as a result of the temperature reached during the firing process, such as differential thermal analysis of thermogravimetry (DTA-TG). In addition, geochemical techniques are employed to determine the chemical composition of a given ceramic material.

The lecture will consist on a concise overview on the use of some of the archaeometric techniques mentioned above, with special concern in examples of historical building ceramic materials such as bricks, roofs, and tiles. The attention will be also focused on main processes and mechanisms of degradation experienced by ceramic materials.

Overall, archaeometric techniques are useful not only to study original ceramic materials and their production technology but also to assess the compatibility of possible reposition materials used in active conservation and restoration works.

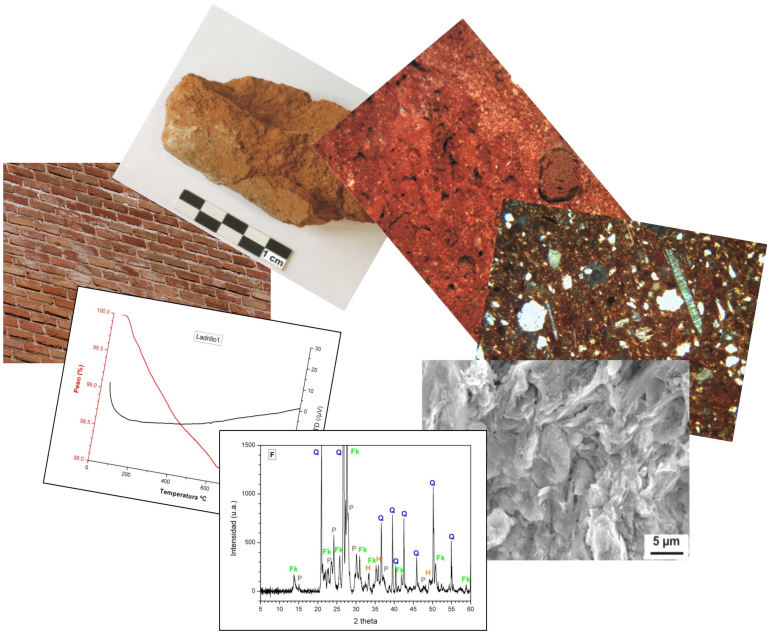

Image 1. Feedback of archaeometric techniques. From brick wall to microscope and so on.

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NON DESTRUCTIVE TECHNIQUES TO MEASURE SURFACE PROPERTIES

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Surface properties refer to the most external section of the materials, which sometimes represents and concentrates the artistic print. It is the original surface and what could be identified as the "skin" of the element or the building. This surface is exposed to the environment and is subject to deterioration. The condition of this interface can be measured with different techniques; when working in cultural heritage non-invasive techniques are advisable. These non-destructive techniques allow the monitoring of the surface properties regarding decay processes evolution and conservation techniques assessment.

1. Introduction

The materials surface is the interface between the material as a whole and the decaying agents. This surface suffers modifications to adapt to changing conditions, which means alteration in natural environments and decay or deterioration in built ones.

These changes in the materials are focused on the surface, and they can be referred to variations in color, texture, hardness and roughness, which implies modifications in petrophysical properties such as hydric and physical-mechanical ones.

Some non-destructive and portable techniques will be detailed in the next sections, as well as some testing procedures to measure properties of the materials. These will be:

- Ultrasounds Pulse Velocity UPV (indirect or surface mode, Vp)
- Surface hardness
- Color
- Surface roughness

Besides materials characterization, the real usefulness of these techniques is that they allow monitoring decay processes and conservation techniques. With respect to decay processes, monitoring can be performed both in real built environments (at different times, in a short or medium term) or in the laboratory, analysing how specific conditions can affect the materials (ice, salt crystallization, fire, etc).

Regarding conservation and restoration methods and interventions the monitoring of the behaviour of materials subject to cleaning, hydrophobization, consolidation, etc., can be assessed, firstly to select the best conservation method to apply to the ceramic material, and secondly to follow in time the materials performance.

2. Ultrasounds Pulse Velocity UPV

There are non-destructive and portable equipments for measuring the velocity of ultrasounds waves travelling through materials. The denser and the more compact is the material, the higher the ultrasounds velocity; on the opposite, the more porous (commonly the more altered the materials), the lower is the UPV. For materials surface surveying, the

direct or surface mode is recommended, consisting of two transducers (emitter and receiver placed in the surface plane/face). In this measuring mode, the wave will travel from the emitter to the transducer just below the surface, in contrast with the direct mode (transducers placed in opposite and parallel planes/faces), in which information of the material bulk is obtained.

This technique is very useful to map the decay condition of any element/structure, and to assess the consolidating effect of some products applied to restore the lost cohesion of materials [1].

3. Surface hardness

There are different ways to measure the surface hardness of materials. In the recent years, equipments originally used for metals, have been developed and adjusted for measuring the hardness of geomaterials used in cultural heritage (stone, mortars, ceramics, etc) [2]. For ceramic materials, the micro rebound tester (Equotip type) is recommended, instead of the Schmidt hammer or sclerometer, both based on the same foundation. The former is more user-friendly and less invasive than the latter, although it can leave in the materials surface some small and light prints, especially in altered or more friable ceramics. As the measured area is a circumference with a diameter smaller than 1 cm, and due to the fact that many ceramic materials are very heterogeneous, a great number of readings are necessary to obtain a representative value.

As well as UPV, it is very useful to monitor processes decay and consolidating treatments. Actually, these two techniques are commonly used together.

4. Color

Color is one of the most obvious properties of ceramic materials, immediately perceived by naked eye. It has been “measured” in a very subjective manner until the more recent use of spectrophotometers, which quantify through chromatic parameters this property. The most commonly colour system used in cultural heritage is the CIELab (1976) [5].

This property can be measured for decay processes (f.i. fire effects), for assessment of cleaning processes, to quantify the undesired colour change after the application of conservation treatments, and in replacement operations.

Figure 1 shows an image of the wide range of bricks attending to their different chromatic properties. In this specific case, many bricks had to be replaced as they were intensely decayed during the Spanish Civil War, and the colour range was measured with a spectrophotometer in order to keep the original appearance of the protected building with the replacing pieces.

5. Surface roughness

Roughness can be seen as the topography of the surface exposed to deterioration. The higher the roughness of a surface – the rougher- the greater specific surface exposed to the environment, deriving in a more rapid deterioration than a polished surface.

The roughness of the materials surface can be measured with a roughness meter. Not all the devices are portable; in the market there are optical roughness-meters, non-destructive, non-invasive and portable, which allows measurements both on-site and in the laboratory.

Image 1. Bricks wall of the main façade of the School of Medicine, Complutense University of Madrid, Madrid, Spain. The wide variety of bricks with different colour can be seen.

Image 2. The variation of colour and roughness of bricks is linked to decay processes. Main façade of the School of Medicine, Complutense University of Madrid, Madrid, Spain.

This property can be quantified using different parameters according to international standards (ISO, DIN).

Especially useful are these measurements when monitoring decay processes and cleaning operations, which commonly increase the value of roughness, favouring an accelerating deterioration of surfaces [6] [7].

6. Conclusions

Petrophysical surface properties are commonly employed for characterization of ceramic materials, assessing the deterioration processes degree and the performance of conservation treatments, allowing monitoring in a short-medium term.

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NON DESTRUCTIVE TECHNIQUES TO MEASURE BULK PROPERTIES

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Bulk properties refer to the whole mass of a system, i.e. they do not depend on the size or the amount of material in the system. Therefore, for these properties to be measured, we need to consider the full object (for example a ceramic piece) to get a significant measurement, as opposed to the case of surface properties. Nevertheless, there are several Non Destructive Techniques that allow determining bulk properties through non-invasive methods. This summary will describe the use of ultrasounds, surface hardness and thermal imaging to determine bulk properties that otherwise could only be determined through destructive testing.

1. Introduction

Bulk properties are inherent to a certain material and by definition do not depend on the size, shape or amount of this material. Once a material is placed in atmospheric conditions and begins to decay, it does not decay isotropically. Decay usually begins from an object's surface. Therefore, in many cases we can find a large ceramic object with a completely deteriorated surface and a relatively intact core. In such a case, bulk properties may not differ that much from those a fresh object could have had (see section 3 of Torraca's book [1] for more details on deterioration of building materials).

Because of this, one of the areas in which bulk properties are particularly relevant is structural materials (i.e. those materials whose purpose is to transmit or support a force). As an example of this, the surface properties of the brick in figure 1 have been modified by intense soiling; however its bulk properties may be still intact. This ceramic piece may have lost aesthetic values, but still be "healthy" in terms of its structural function within the building.

The use of Non Destructive Techniques to measure bulk properties encompasses a conceptual difficulty in comparison with their use to measure surface properties. While surfaces are "accessible", so techniques only need to measure what we already "see", bulk properties need to consider the full object and therefore, we have to extract conclusions about the entire object from surface, non invasive measurements.

Image 1. Historical brick showing intense soiling

In this summary three Non Destructive Techniques that allow determining bulk properties through non-invasive methods will be described:

- Ultrasounds Pulse Velocity.
- Surface hardness.
- Infrared imaging.

2. Ultrasounds Pulse Velocity

Elastic wave propagation in materials is affected by bulk properties of the stone (such as density, porosity, compacity) [2]. Ultrasound pulse velocity technique (UPV) consists of two transducers: one of them emits an ultrasound pulse with a certain frequency and the other receives the signal of this pulse after going through the material. The equipment gives us the "time of transit" of this ultrasonic pulse from the emitter to the receiver. Velocity can be calculated then as:

$$UPV=L/t$$

being L the distance between emitter and receiver and t the time of transit.

The relationship between UPV and the Uniaxial Compressive Strength (UCS) is in the form:

$$UCS = a \cdot e^{b \cdot UPV}$$

where a and b are parameters dependent upon the material properties.

To perform this sort of measurements "direct" UPV measurements (i.e. emitter and transducer face each in opposite sides of the tested specimen) are preferred, and it is necessary to make a specific correlation for the type of tested material.

3. Surface hardness

There are two equipment to measure surface hardness that are often used to determine UCS: Schmidt Hammer and Leeb rebound hardness. Schmidt Hammer consists of a spring-loaded piston impacting against the surface of the sample. The equipment measures the rebound of the piston, which depends on the hardness of the material.

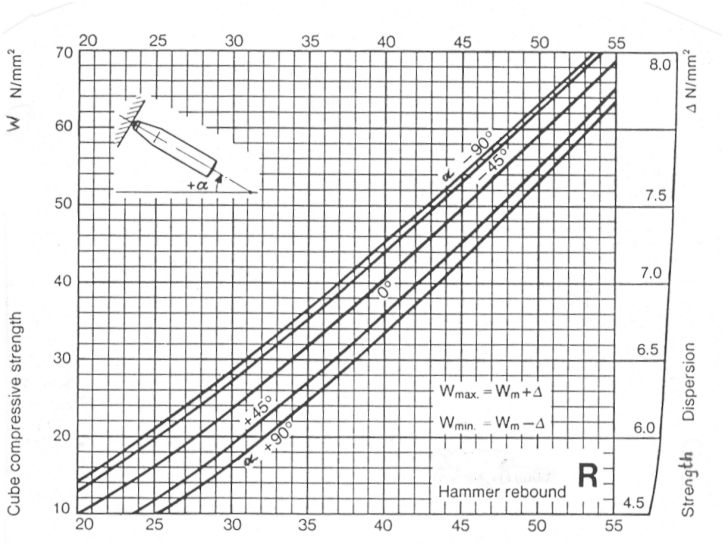

Image 2. Correlation curves labelling an L-type Schmidt Hammer. The curves are designed for Portland cement concrete

Schmidt Hammer was initially designed for concrete testing and equipments normally include a graph correlating UCS and hammer rebound (image 2). This equipment is widely used now in other building materials and despite several factors affecting Schmidt hammer rebound values, there are numerous studies on their effects on the correlation with UCS (e.g. [3]).

Nevertheless, Schmidt Hammer piston impacts very energetically on the tested surface, so it may not be considered “non-destructive”, especially in soft materials. As an alternative, Leeb rebound hardness test is a method developed during last century 70s for measuring metal hardness. Although initially designed for metals, this equipment has been increasingly used for rebound hardness testing of rocks with a focus on correlating Leeb Hardness with Uniaxial Compressive Strength (e.g. [4], [5]).

4. Infrared imaging

Infrared imaging is obtained with infrared (or thermal) cameras and it images apparent surface temperatures obtained from detecting the energy emitted by objects in the infrared spectral range.

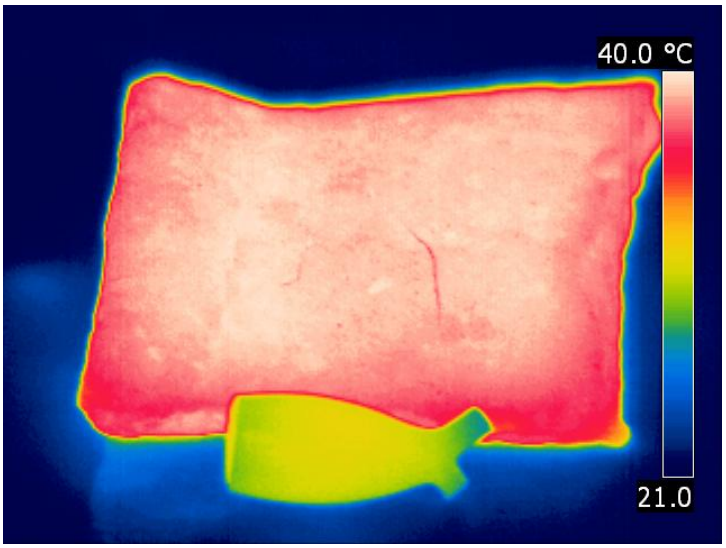

Image 3. Thermal image of 2 ceramic pieces heated to 40 °C to identify internal structural fails through detection of anomalies during cooling.

Infrared thermography epitomises non-destructive testing, as it is non invasive and contactless (reference [6] is one of the most complete texts on infrared imaging). This technique is becoming increasingly cheaper and it is therefore easily available for a wider public.

The image taken by an IR camera depends on the object's temperature, but it is also influenced by material properties, angle, distance, atmospheric conditions, etc. Hence, we refer to "apparent surface temperatures" when describing the images.

Internal structural fails, such as cracks and voids, alter apparent surface temperatures, particularly during heating and cooling. Thermal inertia changes as a consequence of cracks, and therefore a useful method to detect internal cracks in a built structure is to analyse heating or cooling patterns when the building is heated by sunlight. If we are working with samples in laboratory, they can be heated in an oven, and cooling can be monitored with the IR camera to detect anomalies, as it is shown in figure 3.

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TOPIC 4

Intervention/Treatments

DESALINATION OF MASONRY BY POULTICING: FROM LABORATORY TO PRACTICE

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1. Introduction

Salt crystallization is one of the most common causes of decay of porous building materials. Salts can cause damage when they, due to the presence of moisture, undergo crystallization/dissolution cycles. Removing the moisture source can therefore stop salt decay. Unfortunately, this is not always possible (e.g. in the case of masonry exposed to rain) or not wanted (e.g. the invasiveness of air-conditioning systems in monumental buildings). In these situations, desalination, i.e. the extraction of soluble salts from the material, can offer a solution [a.o. 1-2].

2. Decision about desalination

Desalination of masonry is a suitable treatment in those cases where the source of salts is (largely) stopped. For example, if the salt source originates from the use of the building in the past (e.g. as salt storage or as stable), desalination can be an effective solution for the salt problem. Differently, if the salt source is still active, desalination is not a suitable option. Similarly, in those cases where a moisture source, as rain or rising damp, is still present, desalination is not a durable solution. In fact, salt extraction by poulticing (the common desalination method for immovable objects) can extract salts only from the surface of a material (up to a maximum of about 5-7 cm); if a moisture source is present, salts present in depth can still be dissolved and transported to the surface, nullifying the positive effect of desalination. Differently, in case the RH of the air is the main or only moisture source, desalination might still be an effective solution [3].

The most damaging salts are hygroscopic, i.e. they can adsorb moisture from the air when the RH of the air is higher than their RH of equilibrium. This implies that during high RH periods the salts (partially) dissolve and re-crystallize during low RH periods: these dissolution/crystallization cycles cause damage to the material. Salts near the surface react much faster to air RH changes than salts present in depth. Therefore, in those situations where the RH of the air is the only or main moisture source, desalination can significantly slow down the development of salt decay by reducing the salt content near the surface. From the above reported considerations, it is clear that a substantiated diagnosis of the salt and moisture sources is crucial for deciding if a desalination intervention can be beneficial and durable in a certain situation.

It should be underlined that desalination is not only useful for the conservation of the existing (historic) materials, but also for improving the durability of the newly applied restoration materials, which come in contact with the salt loaded substrates. For example, a new plaster will have a longer service life when applied on masonry, which has been desalinated. The application of a

plaster on salt loaded masonry can in fact lead to salt damage within a short time, especially in case the masonry has a high moisture content.

3. Selection of the desalination method

Desalination of movable (heritage) objects can be obtained in a relatively simple way by immersing the objects in water (so-called bath method): because of differences in salt ion concentration (diffusion), the salts will migrate from the salt loaded material to the water. This process is slow, and it requires that water will be regularly refreshed in order to keep the difference in ion concentration between water and object (driver of diffusion) high enough. Depending on the material and on the salt type, it can take months before an object is completely desalinated by diffusion. Moreover, this method cannot be applied to immovable objects, as e.g. masonry buildings.

In the case of immovable objects desalination by poulticing is the most practical option. Poulticing takes place by application of a wet mixture (e.g. cellulose fibres and/or clay and/or sand) on the surface of the material to be desalinated. Sometimes, the substrate needs to be wetted before application of the poultice; in other cases, the desalination poultice itself delivers the water necessary to dissolve the salts. After application, the poultice can be kept wet (wet-poultice) or be allowed to dry (drying poultice). In the first case, desalination will take place by diffusion (the same principle of the bath-method described before); in the second case, salts will be extracted together with water by advection. As advection is a faster transport process than diffusion, the second method is in most cases the most effective (higher salt extraction in shorter time).

4. Selection of a suitable desalination poultice

In order to enhance salt transport by advection, the poultice should fulfil some requirements. First of all, the pore size of the poultice should be smaller than that of the substrate on which it is applied, in order to enhance transport of the solution by capillarity [4], but at the same time not too small, to avoid unnecessary slowing down of the process. Besides, a high total porosity of the poultice is favourable for the transport of the salt solution and the accumulation of the salts. If the poultice does not fulfil these requirements there will be only a minimal transport of salt, mainly due to diffusion (in the period in which poultice and substrate are both wet) and possibly a large part of the salts will migrate in-depth into the substrate. The best results can be obtained by adapting the pore size of the desalination poultice to that of the material to be desalinated [5,6]. Starting from this principle, within a EU research project [7], a modular system of poultices has been developed (image 1). The modular system comprises 4 different classes of poultices: three of the poultice classes are intended for desalination according to the advection principle, one of the classes is intended for a diffusion based wet-poultice. While this last poultice class can be used for all substrate pore size classes, it is however most appropriate for the smallest pore sizes (< 0.1 µm), which cannot be easily desalinated using a drying poultice (table 1). As the desalination poultice chosen according to these criteria has pores smaller than the substrate, water necessary to dissolve the salts will need to be provided before the

application of the poultice, e.g. by spraying. The amount of water should be defined based on the moisture transport properties of the substrate and on the desalination depth, which needs to be reached. In theory, it is also possible to choose a poultice with pores both coarser (to provide water to the substrate) and finer (to extract the salt solution) than the substrate. However, in this case controlling the moisture flows becomes much more complicated; for this reason it can be advantageous to tackle salt dissolution separately from salt extraction.

5. Application of the poultice

Once the necessary pre-wetting has been carried out, application of the poultice (either by hand or mechanically, image 2 left) can start. The poultice is applied in a layer of 15-20 mm and should be left to dry on the substrate for 3-4 days, depending on the environmental conditions (when the poultice is dry, the desalination process stops).

Poultice		**Substrate**			
		micro pores <0.1µm	small pores 0.1-1µm	meso pores 1-10µm	macro pores 10-100µm
Advection	1.		A	P	P
	2.			A	P
	3.				A
Diffusion	4.	A	P	P	P

Table 1. Modular system of poultices : Each poultice class is suitable to desalinate certain classes of substrate pore sizes. A = appropriate extraction poultice; P = possible extraction poultice

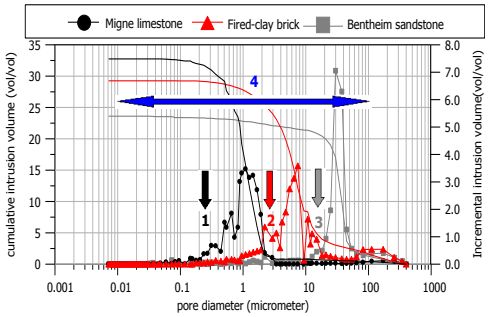

Image 1. Modular system of poultices: the arrows indicate the pore size the poultice should have for each class of pore size of the substrate

In the case of very fast drying (as in the presence of high temperature and/or high air flow) the use of textile sheets on the surface of the poultice can be considered, to slightly slow down the initial drying. Depending on the situation, it might be necessary to repeat the application to obtain a better effectiveness. It is of crucial importance that the poultice maintains a perfect contact with the substrate during the whole extraction process, otherwise the desalination process will stop. In order to guarantee a good contact, a plastic net can be used to press the poultice against the substrate (image 2 right).

Image 2. Mechanical application of the poultice (left) and use of a net for guaranteeing good contact of the poultice with the masonry.

In some cases, it might be necessary to pre-consolidate very weak substrates before desalination can take place. Ethyl silicate (TEOS), a commonly used consolidating product, is however generally not suitable to this scope. In the presence of salts in the substrate, ethyl silicate can remain water repellent (which normally disappears shortly after application) for a long time, making penetration of water, and thus solubilisation and extraction of the salts, impossible.

6. Assessment of the effectiveness of desalination

During desalination, the effectiveness of the process can be monitored by measuring the conductivity of the poultice, as indicative measure of the salt amount. When no significant amount of salt is extracted anymore, the desalination process can be stopped. The salt content in the poultice however, does not provide sound information about the amount and distribution of the salts still present in the substrate. For a better evaluation of the effectiveness of desalination, salt content and distribution in the substrate should be measured before and after desalination, on samples collected at different depths in the material. The effectiveness of the desalination can be expressed as the amount of extracted salt related to the initial salt content. The salt content of the samples should be preferably measured by ion chromatography (IC), as this method provides quantitative information also about the salt mixture remaining after desalination, which might be different from the initial one [8]. Alternatively, in case IC analyses cannot be carried out, salt content can be indicatively assessed by measuring the hygroscopic moisture content (HMC) of the samples at high RH (e.g. 95% RH). The HMC gives a reliable indication of the amount of hygroscopic salts [9, 10]. It is calculated in the following way:

HMC_{95} = 100* (weight sample after storage at 95% RH – dry weight sample)/dry weight sample

The effectiveness of salt extraction (E_i) at each depth (i), can then be expressed as:

Ei = 100* (HMC_{95} before desalination – HMC_{95} after desalination)/HMC before desalination

Image 3 shows the average desalination effectiveness at different depths in masonry desalinated by drying poultices, according to the described principles. The total salt content (measured as HMC) in the outer 6 cm of the masonry significantly decreases after desalination. The highest desalination effectiveness is measured in the outer 4 cm of the substrate. Sometimes, a partial displacement of salts in depth is observed.

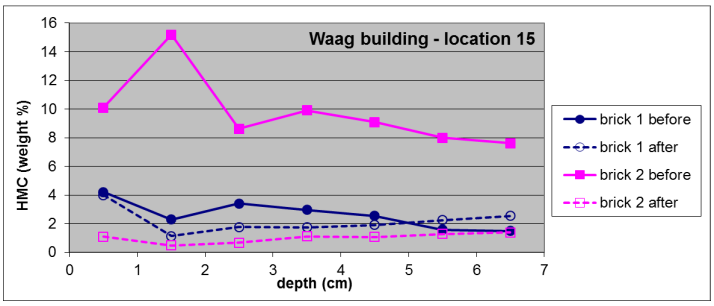

Image 3. Effectiveness of desalination measured after two poultice applications on the masonry of the tower of the St. Andrew Church (Katwijk aan Zee, the Netherlands). Each bar is the average of at least 15 samples at different heights and orientations in the tower.

Conclusions

The use of poultices for extraction of salts from masonry is a well-known treatment in the conservation field. However, the results from practice are often unpredictable. Recent research shows that the effectiveness of desalination can be improved if poultices are designed in relation to the moisture transport properties of the substrate. Preliminary research (diagnosis of the moisture and salt sources, choice of the most suitable desalination method and poultice composition), monitoring during the execution (of the effectiveness) and control after the intervention (effectiveness and necessary additional measures to guarantee durable results) are of crucial importance for the overall success of desalination.

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PROTECTIVE INTERVENTIONS AND TREATMENTS IN HERITAGE BUILDINGS

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The application of new nanostructured and nanoreinforced materials opens a wide field of protective interventions in heritage buildings through the integration of both restorative and conservative actions even in the most aggressive environments. The paper describes an integral approach for the restoration of a heritage building, from the material characterization to advanced interventions to prevent early deterioration of the natural stone attributed to natural events and human actions.

1. Introduction

Generally, the materials and methods carried out in restorative interventions in heritage buildings are based on well stablished technologies and traditional materials. However, these interventions fail when the heritage building is subjected to extreme environments such high solar exposure, high humidity, hurricanes or large concentration of salts or pollutants in the air [1, 2].

The progressive substitution of consolidants and classic water repellent polymers for a new generation of nanoparticle-reinforced hybrid materials turned out to constitute a feasible solution to solve some of the main drawbacks associated to degradation of natural stone used in heritage buildings located in extremely wet areas.

The design of the new material should attend to the required properties. In this sense, the organic fraction of the hybrid material is the responsible of its optical, electrochemical and elastic behavior whereas the inorganic fraction provides the mechanical strength, chemical and thermal stability. Some other aspects such as porosity, hydrophilic and hydrophobic balance and possibility of multiple configurations to achieve the required rheological properties for a suitable application technology are better controlled by a careful investigation on the synthetic methodology.

Nevertheless, for a successful intervention, the external factors affecting the deterioration of the materials should be also considered. Air contamination, extreme thermal variations, rain, humidity, and biologic and anthropic actions may provoke a premature corrosion due to the increased concentration of aggressive components such as CO, CO_2 and SO_2.

Restoration and maintenance works imply a first pre-consolidation stage to prevent further damages. The material should be fully characterized preferably by using non-invasive techniques. This characterization should include not only the structural or chemical parameters but the surface characteristics as well.

Some of the problems associated to the use of non-specific commercial products for the restorative projects abide on surface incompatibilities. These products are generally hydrophobic but they present some permeability to gas and vapor water. In non-silicate rocky

materials it is common to apply a necessary pre-treatment based on silicon compounds in order to achieve the required compatibility between the surface of the material and the consolidant. This pre-treatment usually leads to the precipitation of an undesired crust of CaF_2 and SiO_2. Moreover, when the building is located near to marine areas or industry influence areas, the protective interventions tend to reduce the expected durability because of the action of the corrosive environment.

This work aims to introduce new nanostructured and nanoreinforced hybrid materials in protective interventions in heritage buildings. Our objective is to show the suitability and the multiple possibilities of this family of materials to provide durable and feasible treatments even in the most extreme climatic conditions.

At least it is necessary to stablish 5 necessary stages for a successful protective intervention in heritage building. The first one comprises a thoughtful study of the heritage building (historical documents, plannimetric parameters, etc.) and its comparison with the actual situation. Laser scanning techniques are used to acquire the detailed profile of the actual surface. Afterwards, the substrates were subjected to a deep cleaning process through the application of short laser pulses that lead to the evaporation of the organic substances adhered to the materials surface. Rocky materials were surface and structurally characterized and the original color determination was carried out through spectroscopic characterization.

2. Materials and methods

Hybrid materials prepared through the sol-gel method are composed of an organic network crosslinked with inorganic phases perfectly distributed along the material microstructure. Silanol terminated polydimethylsiloxane (PDMS, Mw 550, ABCR) was mixed with methyltrialkoxysilane (Merck) and a certain amount of titanium alkoxyde or zirconium alkoxyde to produce hybrids materials with biocide and antigraffiti properties, respectively. In the first case, 1-Dodecyl-guanidiniumacetat (Sigma Aldich) was also added to enhance the antifungical activity. Reaction kinetics has been followed through IR characterization. Gelling time and permeability were also analyzed.

The obtained hybrid coatings were applied to different stone surfaces through paint brush technique, dip coating or spraying. The topography of the coated surface was analyzed through atomic force microscopy. The surface characteristics of the different hybrid materials were also evaluated through inverse gas chromatography at infinite dilution.

Fungus growth was determined in petri dishes by using malt extract and optical observation through polarized light in an infrared microscope. The antigraffiti properties were evaluated by spraying a commercial lacquer and its removal was done with a fabric cloth.

3. Results

The evolution of the band corresponding to the hydrolysis of alkoxides allows the determination of the reaction time necessary to obtain a homogeneous hybrid material. Since the hydrolysis is a reversible reaction catalyzed either by acid or organic components, the addition of Zr, which acts as lewis-type catalyst, promotes the formation of the hybrid sol and thus, decreasing the reaction kinetics.

In the same way, we have compared the effect of the two different hybrid materials to evaluate their performance against protective interventions. Gelling time is an important parameter since it is going to determine the whether it still remains in liquid state or, contrary, a viscous gel is formed (Image 1).

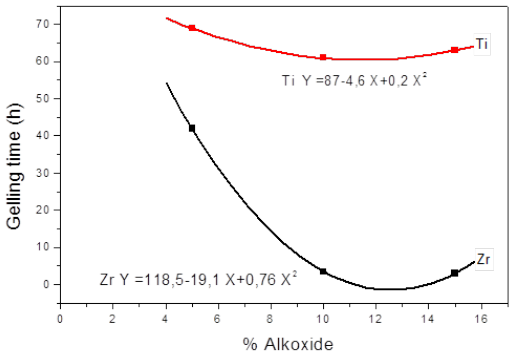

Image 1. Gelling time of a hybrid material as a function of the alkoxide content

Hybrid sols were deposited on stone substrates: marble, limestone and granite (Image 2). The surface roughness goes from 380 nm in the case of bare marble to 50 nm when it is coated through the spray coating methodology. The AFM images also shows that in the case of the uncoated limestone surface, the Δz max is close to 3900 nm but it is reduced to 380 nm in the coated material.

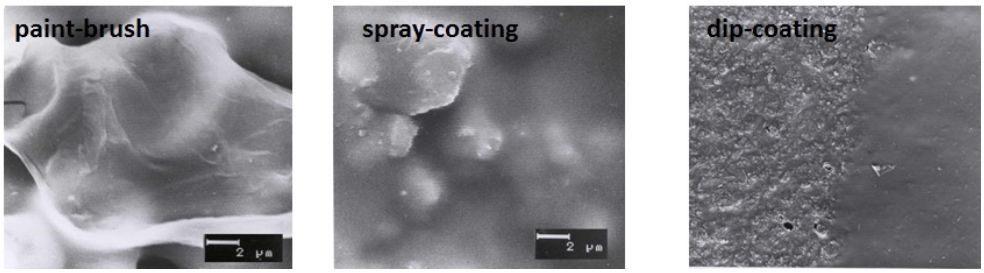

Image 2. Application of the hybrid coatings on a limestone surface

We have determined the surface free energy of the coatings by inverse gas chromatography at infinite dilution and the results are collected in Table 1. It turns out that the increase of Zr in the hybrid material leads to a decrease in the dispersive component of the surface free energy, i.e. it behaves more as a polymeric material rather than a pure silica-

based material. The reduction of the surface free energy due to the presence of the CH_3 groups in the hybrid ormosil coating occurs more progressively that in the case of CF_3 terminals contained in commercial antigraffiti substances (Protectosil) [3].

Table 1. Surface free energy of hybid materials as a function of the Zr content

	γ_s^d (mJ/m^2)		
	5 %Zr	10 %Zr	15 %Zr
50 ºC	67,95	58,66	56,00
60 ºC	49,03	48,15	54,37
70 ºC	50,23	45,73	47,60

After painting with a commercial lacquer, the removal of the painting was complete. After the application of the lacquer, it is observed a continuous shrinkage of the painting until the solvent is completely evaporated. The fabric cloth removes the dried powdered pigment.

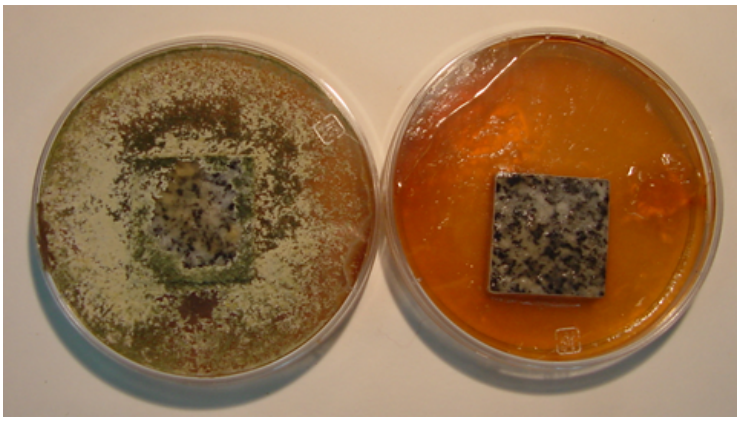

Image 3. Fungus growth in granite in the absence of antifungical ormosil (left) and after application of a thin coating layer of ormosil with 1-Dodecyl-guanidiniumacetat.

Image 3 shows the growth of fungus colonies in a granite sample immersed in malt agar solution whereas in the presence of the ormosil containing the 1-Dodecyl-guanidiniumacetat no traces of fungus were detected after the observation with polarized light in an optical microscope.

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SURFACE TREATMENTS FOR THE CONSERVATION OF HISTORIC MASONRY: BLESSING OR RISK?

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Surface treatments are all those products that are applied on the surface of buildings with the most different aims. Water repellents, consolidants and anti-graffiti coatings belong to this category. In this paper the focus will be on water repellents. Aims, effectiveness, service life and possible risks related to treatment will be briefly discussed.

1. Introduction

Attempts to preserve monumental surfaces from weathering date back to ancient times [1] In the 20th century natural products, like waxes and oils, are increasingly replaced by synthetic chemicals. In countries like the Netherlands there has always been a frequent use of cooked linseed oil for façade protection. In the 1950's, inorganic products (e.g. barium hydroxide [2] and alkali silicates) were progressively substituted by silicon polymers. The development in silicon-based water-repellents, which nowadays are the most frequently used products, is given in table 1 [3]. From silicones to siloxanes to silanes the molecule weight (and size) is smaller, allowing deeper penetration as well as penetration in smaller pores. The end product after polymerization however is always a silicone polymer. The recent 'nano' products have active components of even smaller size (10-9 m) and inorganic components (oxides of e.g. silicium, aluminium or tin) are mixed with e.g. siloxanes [4]; the intention of these products is to improve properties or combine different properties (like water-repellent and biocide).

1.1 Aims of water-repellent treatments

Water repellents are meant to prevent or reduce water penetration in masonry and also to decrease the rate of decay. Additional aims are the prevention of quick soiling and biological growth. A water repellent treatment can also contribute to limit sulfate attack, i.e. the process of transformation of limestone and mortars into gypsum under the influence of environmental pollution: in the presence of a water repellent, sulfuric acid, resulting from the reaction of SOx, present in a polluted atmosphere and water, can not (or at least not easily) react with calcite, which is the main component of limestone and (lime-based) mortars.

Table 1. Historical development of silicon-based water-repellent products based on [Roos et al 2008]

Year	Product	Solvent	Field of application	Active component (%)
1960	Silicone	Organic solvent (White spirit)	Sandstone	<5
1970	Oligomeric siloxane	Organic solvent (White spirit)	Stone, brick	<10
1980	Alkoxy silane	Organic solvent (White spirit) Organic solvent (White spirit)	Idem + concrete	10-100
1990	Mix oligomeric siloxane and alkoxy silane	Organic solvent (White spirit) Water	Idem	<10
2000	Further development above mixes	Idem or as a cream or powder	Idem + use as powder in mortars	25-80
Later	Nanobased products	Mix of ethanol and water	See [De Ferri et al 2011]	

1.2 Working principle

Water absorption in porous materials depends on: total porosity, pore size distribution, pore shape and contact angle between water and the pore wall.

In most porous materials the contact angle is 0° for pure water. In the presence of a water repellent treatment the contact angle increases up to a maximum of 180°, which corresponds to total water repellency (see image 1).

The working principle of a water repellent consists therefore in modifying the contact angle by covering the surface of the pores with a thin hydrophobic layer.

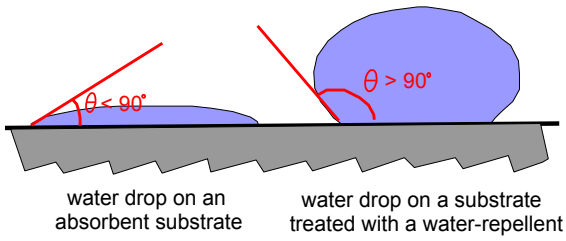

Image 1. Behaviour of absorbing (hydrophilic) and water repellent (hydrophobic) materials.

A hydrophobic compound consists of a polar and a non-polar part: the polar part is attracted by the pore wall, whereas the non-polar part repels the water.

Apart from inhibiting absorption of liquid water, water repellents modify the drying process of a material.

2. Side effects

The drying process of an untreated material occurs in two phases: first by liquid transport and, in a second phase, when the moisture content is lower than a certain value (Critical Moisture Content), by water vapor transport. This is shown by the two different slopes in the drying curve (see image 2a) of an untreated material.

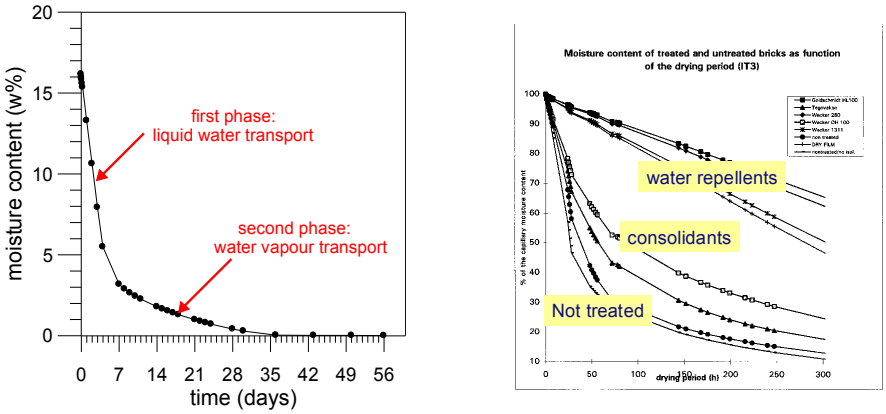

Image 2. Drying curve of untreated brick (a, left). During the first phase the evaporation surface is wet and drying is fast. In the second phase the drying front has moved inside the material and (much slower) drying occurs by vapor transport. Drying curves of treated and untreated bricks (b, right [Van Hees 1998]); for brick treated with a water repellent drying is very slow from the beginning.

Water repellent treatments inhibit liquid moisture transport and have usually a limited effect on water vapor transport. Liquid moisture transport however is much faster than water vapor transfer, therefore drying will occur much faster in the first phase than in the second. As a consequence of the application of a water repellent, drying can occur only by water vapor transport (see image 2b). A dramatic decrease of the drying rate is the overall result.

3. Service life

Although producers of water repellent products very often state that after ca. 10 years the treatment should be repeated, there is no real evidence for such a statement. Research even shows [5] that a much longer service life is possible, in case a treatment has been carried out with care. What however becomes clearly less after a few years is the beading effect of water drops at the surface of the treated material. This is due to the effect of UV light, which however does not affect the treatment directly underneath the surface.

The effectiveness (water repellency) and with that the service life of a treatment can last for a long time, even more than 30 years (see image 3 [6]).

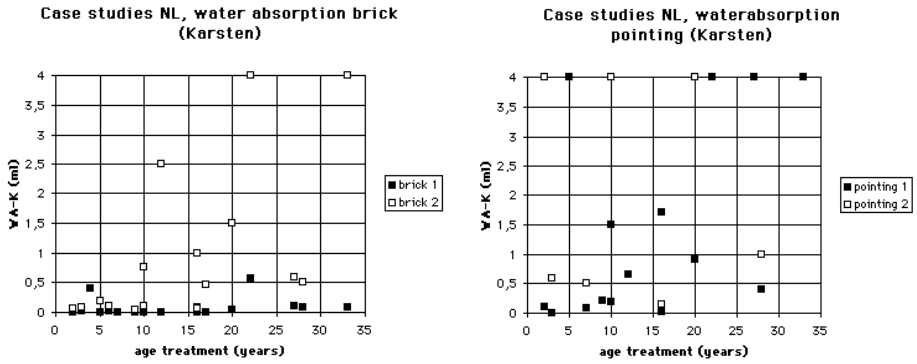

Image 3. Effectiveness of water repellents [Van Hees 1997]. Water absorption (Karsten pipe) on brick and pointing; best and poorest values for case-studies in the Netherlands, assessed as WA-K (ml)= abs. after 15 min. -/- abs. after 5 min., acc. to [Van Hees et al 1995]

Image 3 also shows the following:

-there is no clear relation between the age of the treatment and its effectiveness;

-the effectiveness of the treatment within one building, even within one wall, is quite variable;

-the mortar joint is, from the point of view of water penetration, the weakest part of the (treated) system.

It may be concluded that differences in execution quality as well as the lower effectiveness of the treatment for mortars joints may negatively influence on the overall quality of the treatment. Actually the risk of water penetration still exists, whereas drying will become more difficult. A treatment with defects may then even result in a higher risk of damage, due to for example frost action, than what was the case in the untreated situation existing before.

4. Requirements

Surface treatments should fulfill some of the following general requirements:

-Compatibility: this is the most important requirement, which includes many more specific (technical and esthetical) requirements. Compatibility means that a treatment shall never cause any damage (technical or esthetical) to the historic material. Besides, the intervention must be as durable as possible.

-Reversibility: reversibility means that removal of the treatment should be possible, if necessary in the future. Some anti-graffiti coatings may fulfill this requirement, but reversibility of water repellents is in practice not realistic. One may assume that these treatments, once applied, can never be totally removed.

-Re-treatability: a treatment must be repeatable after degradation of the intervention to an unacceptable level.

5. Risks of treatments

Most of the risks existing are related to the effect the treatment has on the drying behavior of a material (image 2). In case rising damp is present in a wall treated with a water repellent or in case a large amount of water can penetrate in the wall, for example via mortar joints or via little cracks in between bricks and mortar joints, an increased risk of frost damage may occur, due to the slow drying of the masonry.

One of the main risks is the worsening of the damage that occurs if the water repellents are applied on a substrate with a high salt content [5]. As the water repellent inhibits liquid moisture transport, the salts, which can be transported only in solution, crystallize and accumulate just beneath the treated layer. This may result in spalling of the treated zone (image 4).

Image 4. Spalling of the water repellent layer in a brick after a salt crystallization test in laboratory.

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CONSERVATION OF CERAMICS AND BRICKS IN UNDERWATER ENVIRONMENT: STATE OF ART AND NEW PERSPECTIVES

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1. Introduction

The 2001 UNESCO Convention on the Protection of Underwater Cultural Heritage [1] has established the need to protect underwater archaeological sites. The Convention promoted also a cooperation among states to find legal solutions to protect underwater cultural heritage also when it is located beyond territorial waters. By ratifying the convention, each state party undertakes to make use of its own sovereign rights to prevent polluting of archaeological sites and to cooperate with other state parties on this end.

Article 2 paragraph 5 of the UNESCO Convention on the Protection of the Underwater Cultural Heritage states that in situ preservation of underwater heritage shall be considered as the first option before engaging in any activities directed at the heritage site [1]. The convention furthermore encourages the international collaboration among universities, research centers and companies for the purpose of making a significant contribution to protection or knowledge or enhancement of underwater cultural heritage [2]. According to this, recently the activity of underwater restoration significantly increased, leading to new challenges in restoration technologies and strategies. For almost all class of materials, there are quite standardized procedures for their restoration once taken out form the water. In the case of conservation processes taking place directly in underwater, those procedure are obliviously different. In the context of underwater heritage, ceramics represents one the most common stone materials found in submerged archaeological sites. Its abundance is mainly related to the facts that jars and similar were extensively used as containers for goods transportation on ships. Quite different objects, but similar in terms of constituting material, are bricks. They are commonly found in submerged sites close to the coastal line, related to building structures.

2. Subaereal restoration

Generally, the conservation of ceramics and bricks recovered from a marine site is not complicated [3]. When pieces are found encrusted, the most difficult part of the conservation process is the removal of the adhering material without damaging the paste or glaze. For this reason, mechanical cleaning techniques are preferred, but hydrochloric acid is used with some regularity to remove calcareous encrustation. The soluble salts that are present in any porous material recovered from a marine site are removed by rinsing in water. In most instances, tap water is all that is needed, but to the use of de-ionized water in the final baths will remove more soluble salts. Sulfide staining is easily removed with hydrogen peroxide, but other stains, such as iron stains, are more difficult to remove without adversely affecting the material. After drying, object can be consolidated by completely immersing the material in a dilute solution of acrylic polymer. Pottery vessels can be reconstructed after the consolidated sherds have dried.

3. Underwater restoration

Ceramics and bricks that have to be restored and conserved into the underwater archeological site need a different approach. One of the main issue related to pottery conservation is related to the biological colonization, which occurs on the stone surface. Its removal is often very difficult due to the high mechanical resistance of the encrustations.

Recently a project funded by the Italian Ministry of Education and Research (CoMAS -In situ conservation planning of Underwater Archaeological Artifacts – www.comasproject.eu) was aimed at the development of new materials, techniques and tools for the documentation, conservation and restoration of underwater archaeological sites in their natural environment. In particular, in the context of the project, a goal was the development of new cleaning and restoration electric tools that make easier and faster the work of the underwater restorers. The project test-bed is the Marine Protected Area - Underwater Park of Baiae that is located in the bay of Pozzuoli (district of Napoli) and stretches out in the sea for 176.6 hectares. The area includes the shores of Baiae and Pozzuoli, between the southern pier protecting the harbour of Baiae and the pier of Lido di Augusto, immediately east.

The park is known worldwide for its phenomenon of bradyseism, in fact the coastline of Roman age is currently submerged below the present day sea level, the rests of the harbour structures and of the ancient town ruins of the same age are currently at a depth varying from 1.5 m to 15 m along. The new tools have been specifically designed in order to satisfy restorers' needs that occur during the subsequent phases of the cleaning work performed, during the in-situ restoration process, on the submerged artifacts. In particular, several electromechanical underwater tools have been developed: an electric cleaning brush tool to remove the loosely adhering deposits; a small electrical chisel to allow restorers to proceed the cleaning process with the removal of tightly adhering deposits; and, at last, an electrical hand-held grinding tool in order to achieve a complete removal of all the materials that cover the remains without damaging their surfaces [4].

Another issue related to the underwater conservation of surfaces is related to the mitigation of the biological growths on the cleaned surface. In fact, once removed, the biofouling is quickly reformed. For this purpose, another section of the CoMAS project was focused on the formulation and the testing of new protective products for preventing the biological growth. Innovative formulations with antifouling properties have been setup and then, their effectiveness were investigated on pottery specimens arranged in seawater and monitored over time. Results indicated that treatments were able to slowdown the biological colonization.

These research outputs can boost the interest into underwater restoration, leading to the elaboration of more efficient, cheaper and more sustainable restoration procedures.

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TOPIC 5

Preventive conservation

PREVENTIVE CONSERVATION OF BUILT HERITAGE

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1. Introduction

Preventive conservation develops a systematic working methodology that allow us to detect and control the deterioration processes affecting cultural property. This concept of heritage conservation represents a strategic change and has been present for several decades now, with this or another denomination, nationally and internationally promoted by authors like De Guichen [1], Michalski [2], De Tapol or Herráez & Rodríguez Lorite [3].

In our country, in 2011 the Ministry of Education, Culture and Sports, through its General Branch of the Institute of Cultural Heritage of Spain (IPCE) promoted a National Plan for Preventive Conservation (PNCP) to implement the use of a different methodology of that employed so far in preserving the extensive Spanish cultural heritage [4]. This article outlines the basic principles of the proposed method, with particular emphasis on the most relevant issues concerning built heritage.

2. Conservation: preventive conservation, remedial conservation and restoration

The ICOM-CC published *Terminology for Defining Conservation of Tangible Cultural Heritage* (New Delhi, 2008) [5]. This text defines conservation as all those measures and actions aimed at safeguarding tangible cultural heritage. Restoration being understood as all those actions whose purpose is to facilitate the appreciation, understanding and use of the building, whereas remedial conservation is taken to mean all those actions designed to halt harmful processes or to strengthen the structure.

Preventive conservation are those measures or actions designed to prevent or minimize future deterioration or loss, which are performed on the surrounding area or environment. These measures and actions are indirect - they do not interfere with the materials and structures of the items. They do not change their appearance. We found a similar definition in the european standard *Conservation of Cultural property. Main General terms and definitions* (EN 15898, 2011).

The PNCP addresses this conservation strategy from a broader perspective and proposes a method of systematic work to *"...identify, asses, detect and control the deterioration risks in cultural property , in order to eliminate or minimize these risks, acting on the source of the problems, which are usually found on the external factors to cultural goods themselves, thereby preventing deterioration or loss, and avoiding the need to undertake future drastic and costly treatments on the works themselves..."*

The plan also considers other aspects that must be taken into account as are *"...sustainability, resource optimization and accessibility, understood as an approach of cultural property to society, all of them concepts that impact positively on improving the heritage conservation status…".*

This strategy aims, as De Guichen said in the case of Altamira Cave Preventive Conservation Plan [6], *"... to coordinate and implement a set of systematic strategies, organized in time and space, developed by an interdisciplinary team with the consensus and participation of the community in order to preserve, protect and disseminate the collective memory in the present*

and project it into the future, strengthening their cultural identity and raising the quality of life ... ".

A preventive conservation plan is conceived as a management tool to define and articulate the conservation strategy in the short, medium and long term, and thus ensure the survival of the work. Therefore, it is considered to be an open document, which must be reviewed and updated based on the achievement of objectives, and the needs cultural property preservation demands.

3. Working methodology: development of a Preventive Conservation Plan (PCP)

This conservation strategy is based on identifying the risks detected during the study of the cultural property, in the definition of actions to avoid, block or reduce them. Given the complexity usually involved in the conservation of cultural property, the goal is to develop a tool that serves to implement procedures for monitoring and controlling the risks of deterioration, of the protocols of scheduled maintenance on the property, establishing an organizing model to assign roles and responsibilities among the different agencies, organizations and professionals involved in their conservation. For the design of a preventive conservation plan, five phases have been established:

The first phase is a documenting phase, beginning with the study of cultural property to be conserved, its conservation condition, its use and management, and all information concerning the institution. The material history of the building has to be added to all of this, with data on materials, their nature and alterations, the building systems, the location environment, the inventory of assets under the plan, their conservation condition and finally, an analysis of vulnerability and significance. The documentation and research process should not be limited to a preliminary stage, but should be an ongoing process [7].

In the second phase, which will be based on the acquired knowledge about the cultural property, analysis, identification and assessment of alteration risks are undertaken, priority setting regarding methods of monitoring and control, and if necessary, its use regimen or accessibility. It is also necessary to define curative conservation treatments or restoration to be carried out.

The risks may have different cause and origin. Citing again De Guichen [8] we could talk about risks arising from human activity (fault or negligence in management, erroneous tasks, and impact of government) and natural hazards such as biodeterioration that is generally associated with poor environmental conditions and deficiencies in the provision and maintenance of facilities. The effects of the various risks may be immediate and catastrophic (natural disasters, antisocial acts, fires, floods) or slow and cumulative (inadequate temperature and humidity, radiation associated with light, air pollutants).

Once this phase is completed the third one can be addressed, proceeding to the design of procedures for monitoring and control of risks, including monitoring of environmental parameters [9] and the development of protocols for action, which should include various tasks such as maintenance of technical installations. The goal is to plan a series of systematic measures or routines that will allow kicking off a prevention strategy and implementing to last through time. The design of these procedures must take into account the available resources, the definition and degree of involvement of the different professionals, belonging to the institution or external to it, the definition of technical means and working procedures, and planning scheduled performances, with special attention on the measures to be taken in

emergency situations. It is essential to plan the use and management of the cultural property, consistent with its conservation.

The fourth phase is the implementation phase of the plan, of its organizational model, which must be preceded by a training and motivation program of the professionals involved, which will allow to start procedures and protocols, if they had not been already activated, and adapt all them to the daily difficulties that may appear. Programming and coordinating of both action and personnel involved, will be the cornerstone for the implementation of any preventive conservation plan.

Accordingly, a communication and outreach program should be started, which will seek awareness and community involvement in the conservation of cultural property.

The last phase is the verification phase and consists on the periodic evaluation of the plan after implementation, incorporating the necessary improvements. The pursuit of excellence, involves conducting internal and external audits, with the possibility for them to be associated with quality management systems (ISO 9001).

This verification should be done within two or three years, provided the conditions do not substantially change as to require a new risk analysis.

Meanwhile, the staff responsible for implementing the plan must make a continuous and periodical verification of the established procedures, the satisfaction degree of society, and of the institution staff in relation to the PCP.

Finally, I would like to thank Concha Cirujano and Juan A. Herráez, Division of Preventive Conservation from the Research and Training Area at the IPCE, for the review and contributions to this text.

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TOPIC 6

Case of study

IMPROVING THE KNOWLEGDE OF CERAMIC MATERIALS MANUFACTURE BY MEANS OF ANALYTICAL TECHNIQUES

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1. Introduction

Clay versatility is enhanced by the use of additives that enable the improvement of certain properties [1, 2]. Firing clays involves mineral phase changes that mainly depend on its composition, heating rate, maximum firing temperature, remaining firing time and oxidation or reduction kiln conditions [3, 4]. The firing temperatures reached can be deduced from the presence or absence of certain mineral parageneses [5]. Mineralogical variability is greater during firing in calcium-rich clay than low-calcium content clay [6].

Ceramic materials used at Former Workers Hospital of Maudes (Madrid, Spain), built between 1909 and 1916 by Antonio Palacios Ramilo (1874-1945), are studied. The building mainly consists of four bays arranged diagonally around several gardens, with a fountain in the central one. The brickwork walls comprise outer face stonework shaped mainly with limestone and some original staircases of the gardens are made of bricks. The building façades as well as the body of the fountain are decorated with ceramic pieces and the fountain basin is adorned with a tile *trencadiç*. At 80´s, nearly all the original ceramic pieces on façades were replaced and the fountain *trencadiç* was partially repaired [image 1]. Decorative ceramics used inside the building should be taken into account, as fountain tile *trencadiç* manufacture is probably connected with these materials.

References related to decorative ceramics [7-9] noted that original ceramic pieces were made by Daniel Zuloaga in Segovia (Spain) with iron oxide-rich red clay and silica added and were fired in an oxidising atmosphere at 1200 °C; that the original tiles for the basin fountain were pressed and manufactured by a Spanish Eastern or Sevillian (Spain) company; and that the interior decorative ceramics were processed by Ramos Rejano in Seville.

Such references also pointed out that at 80´s the replaced ceramic pieces of façades were mechanically pressed, using Madrilenian clay and sand from Segovia, grog from Teruel (Spain) and high quartz content as additives and they were fired under oxidising conditions at 1200-1250 °C; and that tiles used to repair the fountain tile *trencadiç* (made by extrusion) as well the inner decorative ceramics (by semi-mechanical pressing), were made from red mud, calcium-rich pastes and Madrilenian sand at Madrid's School of Ceramics and were fired at 1030 °C.

By means of optical microscopy and X ray diffraction analysis, bricks of inner walls and gardens staircases (both originals) and decorative ceramics (originals and made at 80´s) are studied. Findings of the analyses conducted are compared with the references consulted and new data on manufacture of ceramic materials found in a heritage building are provided.

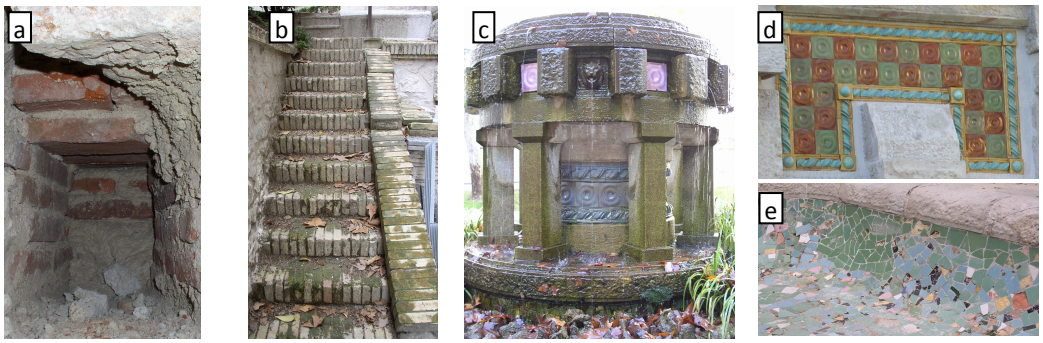

Image 1. Ceramic materials at Former Workers Hospital of Maudes (Madrid, Spain). Original bricks that shape inner fabric walls (a) and staircases of gardens (b); original ceramic pieces that decorate the body of the fountain (c); replaced decorative ceramic pieces on façades (d); tile *trencadiç*, original and repaired (upper area, with green color), that cover the fountain basin (e).

2. Results and discussion

2.1 Optical microscopy analysis

Image 2 displays polarized optical micrographs of the ceramic materials studied, where aggregate mainly comprised monocrystalline quartz grains.

The inner fabric wall bricks show significant chromatic and textural heterogeneity and high porosity, mainly due to its firing under uncontrolled atmospheres and its manual pressing, possibly at brickworks that were then located nearby the hospital [10]. The gardens bricks were carefully manufactured and the addition of generous amounts of grog, which enhance paste strength and avoid contraction during firing [2], can be observed.

Original ceramic pieces show grog and quartz aggregates with heterogeneous size as well as opaque minerals, possibly iron oxides from the red clay used [7], are observed. In both the original and replacement ceramic pieces, the important amount of quartz grains aggregates would confirm that silica was added to the original pastes and Segovian sand to the replaced material [7], mainly as a degreaser to improve the mechanical properties of the pastes [11].

The even texture observed in the replacement ceramic pieces, in terms of aggregate size and shape and of its orientation parallel or sub-parallel to the outer surface, was due primarily to the mechanised manufacturing procedure used [7]. In the original tiles, the aggregate: paste ratio is 1:3 and 3:1 in the repair material; this could point out that stronger pastes achieved by adding aggregate inclusions of quartz were employed at repaired tiles manufacture.

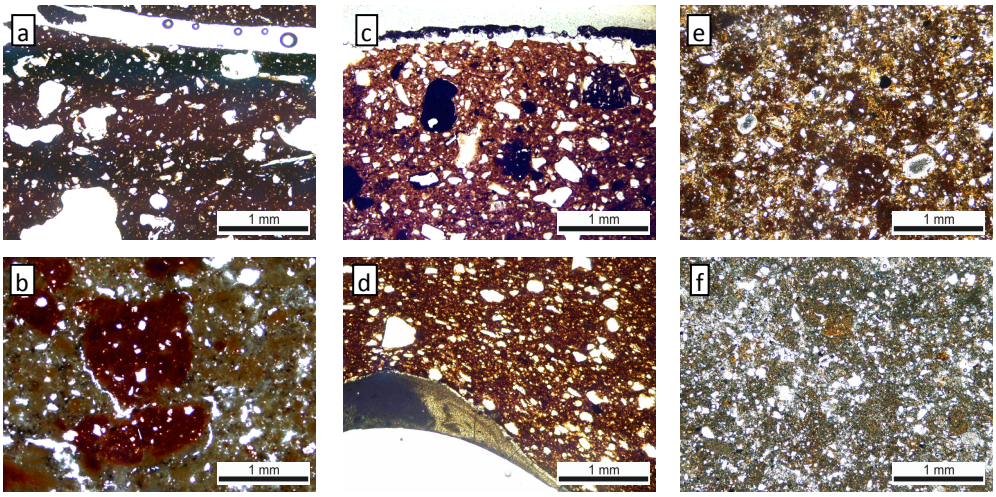

Image 2. Polarized optical micrographs of the ceramic materials studied (plane polarized light). Original bricks, from inner fabric walls (a) and staircases of gardens (b); original ceramic pieces that decorate the body of the fountain (c); replaced ceramic pieces on façades (d); original (e) and repaired (f) tile *trencadiç* that cover the fountain basin.

2.2 X ray diffraction analysis

Mineral phases identified by X ray diffraction are shown at image 3. At inner fabric walls bricks, the presence of hematites would reveal the existence of iron oxides in the clay raw material and/or they may have also been generated during firing [12]. The identification of gehlenite and anorthite would denote the use of a mix of kaolinitic and calcitic clays, in which, during the firing process, metakaolinite-gehlenite-anorthite recrystallisation would have taken place.

This reaction would have been enhanced by the structural similarity among these three mineral phases and expedited by the replacement of the aluminium in the kaolinite with iron [13]. The detection of gehlenite and anorthite would indicate that the temperature reached must have been over 950 °C. The high temperature mineral paragenesis identified in the gardens bricks (large amounts of wollastonite, diopside and anorthite and the near absence of gehlenite) reveals the use of a technology able to reach temperatures of over 1000 °C.

Firing temperatures reached for ceramic pieces, 1200 °C for originals [9] and 1200-1250 °C for replaced [7, 8] could not be confirmed. Nevertheless, since quartz concentration declines drastically from 1100 °C [14], the high quartz content ruled out firing temperatures of 1200 °C in the fraction analysed.

In the ceramic pastes used in gardens bricks and fountain original tiles, the absence of phyllosilicates and carbonates as well as the presence of wollastonite, gehlenite and diopside pointed out that the firing temperatures must have been higher than 900 °C and that the clay raw material had a high calcium and/or moderate magnesium content [6, 14]. This could denote that both ceramic materials could have been elaborated from the calcium-rich clay used at Sevillian traditional ceramic industry [15], so they could be manufactured by the same company (Ramos Rejano) that made the interior decorative ceramics. Besides, mineral phases identified at repair tiles pastes may confirm they were made with calcium-rich pastes and that the firing temperature was around 1030 °C [7]. The failure to identify anorthite and the presence of gehlenite and wollastonite in the repair tile pastes might be attributed to a low calcium or silica content in the clay used in their manufacture [9].

These high temperature (≈800-1000 °C) or neoformation mineral phases were generated in the clay paste during firing when the phyllosilicates in the clay raw material reacted with the calcium or magnesium oxide released during calcite or dolomite decomposition [16]. The presence of gehlenite and diopside together denotes firing temperatures of over 900 °C, while gehlenite alone is indicative of temperatures of over 800 °C and much higher than 900 °C if wollastonite is generated [16]. Diopside forms at higher temperatures than gehlenite and its presence entails the partial disappearance of the latter [15]. Gehlenite and wollastonite are regarded as intermediate compounds [17, 18] that became unstable phases in the presence of silica and high temperatures, generating neoformation phases with a higher silica content such as anorthite [6, 14, 16].

The intensity of the main diffraction peaks of the high temperature mineral phases may serve as grounds for establishing differences in the firing temperatures reached. The original tile pastes (Gh > Di, Wo and An) were therefore fired at a lower temperature (>800 °C) than the repair tile pastes (Gh ≈ Di and Wo; >>900 °C), which were in turn fired at lower temperatures than the gardens bricks (Gh < Di, Wo and An; >1000 °C).

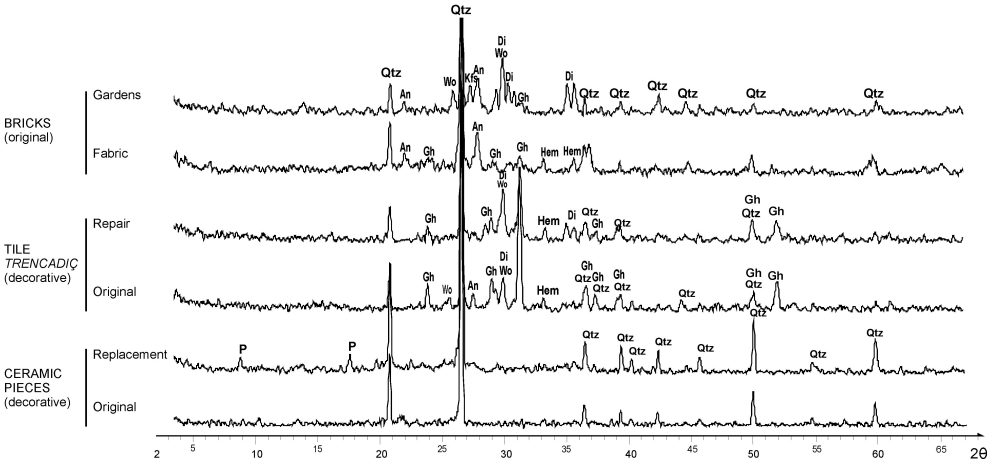

Image 3. Mineral phases identified by X ray diffraction on ceramic materials pastes (P: phylosilicates, Qtz: quartz, An: anorthite, Gh: gehlenite, Wo: wollastonite, Kfs: potassium feldspar, Di: diopside, Hem: hematite).

Conclusions

Inner fabric walls bricks and decorative ceramic pieces made by Zuloaga displayed uneven textural features, corresponding to their manual processing. Similar mineral parageneses identified at bricks from gardens and original tile *trencadiç* noted that they could be elaborated from related clay raw material and were probably manufactured by the Sevillian company that made the interior decorative ceramics. In order to increase the ceramic pastes strength, the manufacture of the materials studied carried out the use of grog and quartz aggregate inclusions as additives as well as firing temperatures circa 1000 ºC.

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CERAMIC CHARACTERIZATION OF PORCELAIN FLOORING TILES FROM LA CASA DEL LABRADOR IN ARANJUEZ

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Most probably the two porcelain tiling floors in La Casa del Labrador are the unique historic porcelain floors in Europe. Nowadays and worldwide, porcelain tiles is one of the most outstanding productions in the ceramic sector, but this is just a recent development if considered that porcelain was created in China almost two thousand years ago and that porcelain began to be produced in Europe in the eighteenth century. Except porcelain tower at Nanjing, China never considered porcelain as a building material and in Europe only Capodimonte and Buen Retiro employed porcelain as an architectural material in the three porcelain rooms built for the royal palaces of Carlos III in Naples, Aranjuez and Madrid.

Twenty nine shards, remains of a past restoration of the Casa del Labrador, were analyzed (XRF, XRD and SEM-EDS) to determine their elemental and mineralogical composition and their microstructure. Porcelain tiles consist in a dense magnesian hard paste body cover with a 100 – 150 µm tick feldspathic glaze. Decoration with colored enamels was over-glaze painted.

Ceramic characterization provides not only information about main features in order to ascribe ceramics to a manufacturer or an epoch, but also to determine how, and even why, ceramics were done. The aim of this presentation is to indicate how microstructure, considering components and interfaces, determines in addition the wearing and decay of ceramic building materials.

1. Introduction

1.1 Porcelain tiles

Porcelain, a white, strong, vitreous, translucent and resonant material, is the most outstanding of all traditional ceramic productions. The academic approach to porcelain includes its triaxial formulation with 50 % of kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), 25 % of potassium feldspar ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$) and 25 % of quartz SiO_2 and its heating a high temperature (1250 – 1400 ºC) to produce a dense microstructure where a network of mullite ($3Al_2O_3 \cdot 2SiO_2$) crystals and relics of quartz grains are embedded in a continuous glassy phase [1, 2].

This microstructure gives to porcelain its exceptional technical properties, such as low water absorption or superior mechanical strength, and its appreciated aesthetic appearance if compared with earthenware products. However, with very few exceptions, porcelain was not considered as a building material until around thirty years ago Modified formulations of the basic composition, innovation in raw materials treatment and forming process, and fast firing cycles (60–90 min cold-to-cold) at quite low (1200 ºC) temperature make porcelain tiles highly competitive as roofing, cladding and flooring elements [3]. Porcelain tiles, with improved wearing resistance or even additional functionality, have displaced earthenware and majolica traditional tiles becoming an essential component of leading and sustainable architecture [3, 4, 5, 6].

1.2 Buen Retiro Factory

Flooring tiles to pave two rooms in the Casa del Labrador was one of the last assignments of the Real Fábrica de Porcelana de Buen Retiro before the factory was closed and dismantled as a result of the Napoleonic War in 1808. Buen Retiro had been producing porcelain since 1760, when Carlos III inherited the Spanish throne and closed the Capodimonte Manufactory (1743 – 1759) [7]. Buen Retiro (1760 - 1808) produced initially the same soft paste porcelain that had been fabricated in Naples, but soon afterwards new formulations were introduced to adapt local raw materials or to improve the quality of its productions. Like all Europeans manufacturers, Buen Retiro made innumerable efforts trying to find the *petuntse* and the *kaolin* to achieve pastes similar to Chinese or Saxon porcelains.

1.3 Bartolomé Sureda and the magnesian hard paste porcelain

Bartolomé Sureda (1769–1850) was appointed technical director of Buen Retiro in 1803, when he was training the French porcelain production at Sèvres. After tried diverse clays and earths, Sureda achieved a new hard paste using the triaxial composition bearing quartz, feldspar and clay, but substituting sepiolite ($Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$) instead of kaolin [8, 9, 10]. Sepiolite, known at that time as “tierra de Vallecas”, is a refractory clay quarried near Madrid that had been previously used by Buen Retiro in one of its worst productions, when local raw materials were started to be used to prepare the soft paste. However, sepiolite hard paste, cover with a feldspathic glaze and fired above 1300 ºC, was a success and tableware and tiles were massively produced.

Image 1. (a) the polychrome porcelain tile floor in the *Sala de Compañía* of La Casa del Labrador; (b) and (c) the twenty nine tile shards, stored in the palace, that were choose for study.

2. Sampling and methodology

Twenty nine different colored fragments (Image 1, b and c) of tiles were chosen between the remained pieces from past restorations that were stored in the palace. All fragments could be identified in the designs of the floors that still cover two rooms of La Casa del Labrador. The availability of these damaged pieces allowed carrying out the analyses of samples larger than those employed in the minimally invasive tests.

Elemental composition was determined by X-ray fluorescence using a spectrometer (XRF - MagiX PW 2424, Philips). The structure of crystalline phases in bodies and enamels was determined by X-ray diffraction in a (XRD - Siemens D 5000) diffractometer with Cu-Kα (0.15418 nm) radiation. Relative abundance of crystalline phases in the body was estimated by the Rietveld method.

The microstructural analysis was carried out using a field emission scanning electron microscope (FE-SEM - Hitachi 4700) fitted with an energy-dispersive spectrometer (EDS – Noran). Standardless quantification, using an EDAX-ZAF correction procedure, was performed in spots (1-2 µm diameter) and in areas (~ 300 x 400 µm) and glaze (~300 x 100 µm) of porcelain bodies.

3. Ceramic characterization

SEM microphotograph (Image 2, a) shows, in a transversal section, the layered microstructure of porcelain tiles. From right to left, the highly dense porcelain body, the thick, 100 to 150 µm, glaze layer and the thin, 6 – 20 µm, colored enamel layer.

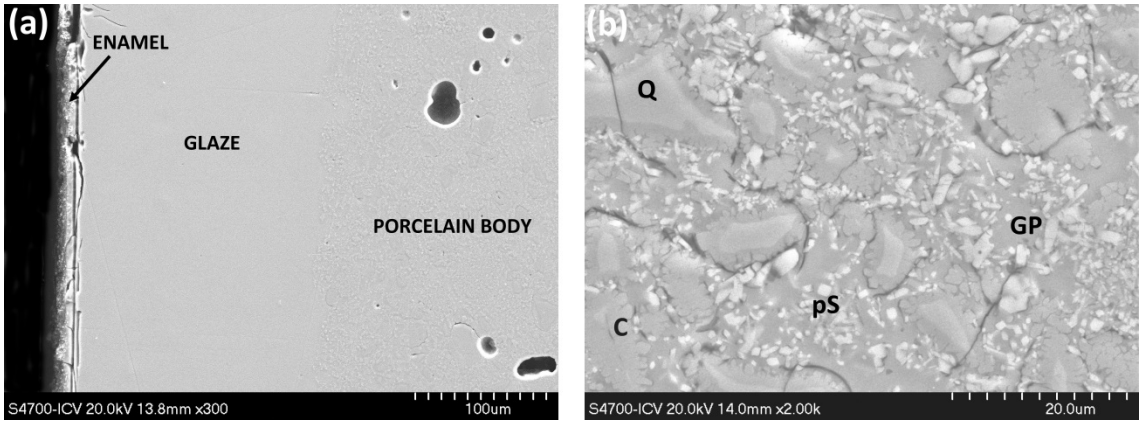

Image 2. (a) Representative transversal section of a glazed and enameled porcelain tile. (b) Microstructure of the porcelain paste showing the glassy phase (GP) and the dispersed grains of quartz (Q), transformed in cristobalite (C) in the borders, and the small crystals of proto-enstatite (pS).

3.1 Porcelain hard paste

The chemical composition of the porcelain bodies (Table 1) is very consistent with the Sureda's magnesian hard porcelain that have been found in the shards of tableware, sculpture and also tiles recovered in the archaeological prospection of Buen Retiro site [10]. Sureda's porcelain is characterized, if compared with contemporary European porcelains, by the presence of a significant, between 6 and 17 %, amount of magnesium (MgO) and the high silica (SiO_2), between 75 and 83 %, and the extremely low alumina (Al_2O_3), between 4 and 6 %, concentrations.

X- ray diffraction indicates three crystalline phases: α-quartz (SiO_2), α-cristobalite (SiO_2) and proto-enstatite ($MgSiO_3$) in quite variable amounts, but glassy phase content remains almost constant, about 55 %, as noted in early studies [8.9]. Microstructures observed in the scanning microscope, Figure 2-b, confirm the elemental and mineralogical analysis. Porcelain consists in a continuous glassy matrix where crystalline phases, α-quartz, α-cristobalite and proto-enstatite, are dispersed.

Table 1. Average values (% wt) and standard deviations of body and glaze compositions in porcelain tiles.

		Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
Porcelain bodies								
XRF	*mean value*	0.8	12.2	4.9	79.3	1.8	0.6	0.3
	σ (n=5)	0.3	4.8	1.1	3.8	0.4	0.4	-
EDS-SEM	*mean value*	0.8	13.0	4.2	79.2	1.7	0.1	0.2
	σ (n=7)	0.3	0.4	0.6	1.7	0.3	0.1	-
Glazes								
XRF	*mean value*	2.9	0.6	18.9	67.8	8.1	1.1	0.2
	σ (n=10)	0.3	0.3	0.9	2.7	1.6	0.4	
EDS-SEM	*mean value*	4.0	0.9	18.6	68.8	6.8	0.6	0.2
	σ (n=7)	1.1	0.6	1.4	1.7	1.9	-	-
Meissen Glazes (Domoney,2012)								
EDS-SEM		0.9	0.1	16.4	73.8	3.7	4.3	0.8
		0.3	-	1.2	1.8	0.7	1.4	0.3

These results are in very good agreement with the recipe "*for the tiling of la Casa del Labrador*" that includes "*tierra de Vallecas*", flint and feldspar in the Sureda's notebook [11].

3.2 Glaze

Porcelain tiles are cover with an uncolored and transparent glaze that appears in the SEM image (Figure 2.a) as a 150 – 250 µm tick homogenous layer. Chemical analyses were performed with XRF on the external surface and with SEM-EDS on the cross section of the samples (Table 1). If reduce to the usual molecular glaze formula: $RO{\cdot}Al_2O_3{\cdot}SiO_2$, where RO are the flux oxides (alkaline, alkaline-earth), glaze composition yields in the formula $RO \cdot 1.1\ Al_2O_3 \cdot 6.7\ SiO_2$ which corresponds to natural feldspar ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$). Maturing temperatures, as high as cone 11 (1300 - 1320 ºC) can be inferred from the glaze composition [12]. Data of Meissen hard paste porcelain glazes [13] (Table 1) were recalculated as RO · 1.2 Al2O3 · 9.2 SiO2 with a slightly higher maturing temperature: cone 13 (1336 - 1356 ºC).

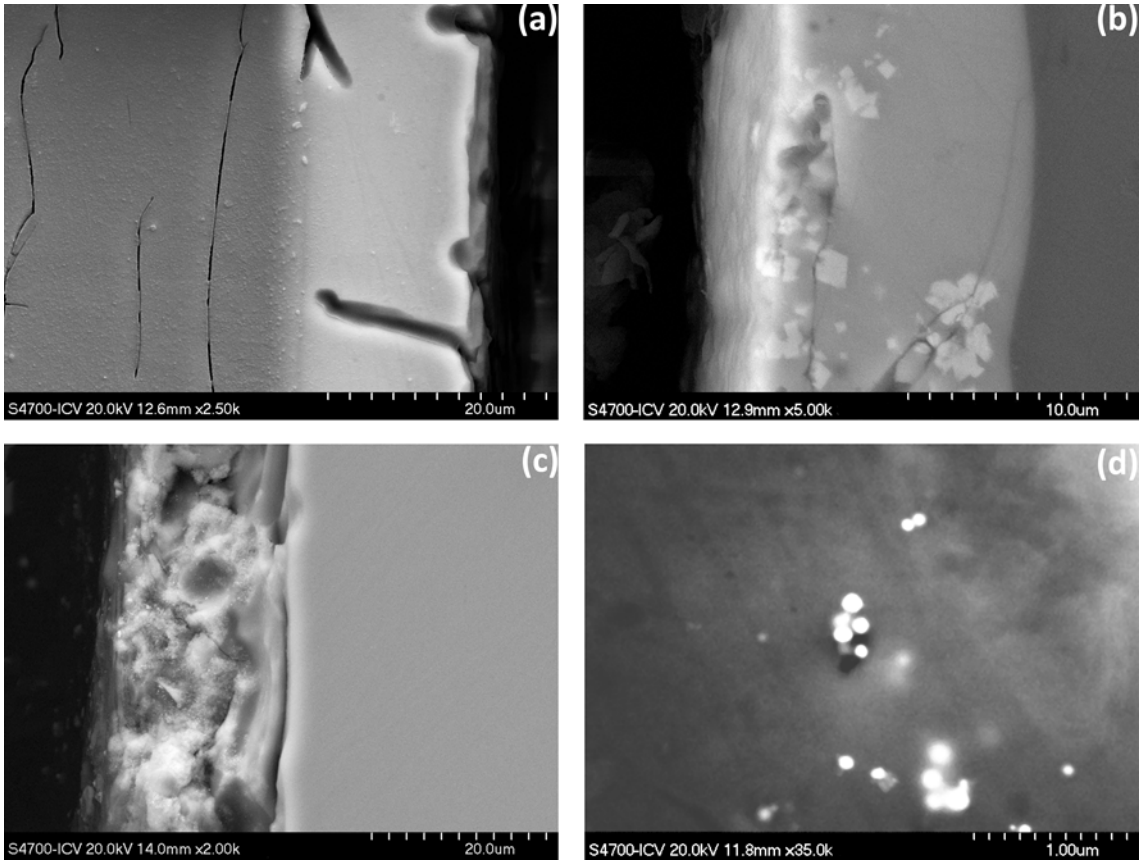

Image 3. SEM micro-graphs of cross sections of enamels. (a) A vitreous blue enamel consisting in a Co-colored frit (right) and the underlying glaze (left). (b) Lead antimonate crystals precipitated into a yellow enamel. (c) Red enamel, based on Naples yellow plus Cassius purple, clearly separated from the feldspathic glaze. (d) Gold nanoparticles into a violet enamel containing Cassius purple.

3.3 Overglaze enamels

The enamel, observe in Image 2-a and, with more detail, in micrographs a, b and c of Figure 3 is a thin layer of colored glass deposited over the glaze surface. Enamel consists in a high PbO - SiO_2 frit, called also flux, where pigments are disperses. Up to fourty seven different hues and shades were identified in the tiles palette. However all the colors were obtained by mixing five basic pigments: green from cooper and blue from cobalt, which are present as ions in the glass network, and Naples yellow, Cassius purple and black from manganese and iron which appear as aggregates of minute crystals dispersed in the frit. These crystalline phases were identified by XRD on the tile faces: tin-doped lead antimonate ($Pb_2Sb_{2-x}Sn_xO_{2-x}$) with pyrochlore structures in the yellow; Mn-Fe mixed oxide with cubic structure equal to mineral bixbyite ($Mn_{2-x}Fe_xO_3$) in the black; and face-centered cubic metallic Au plus cassiterite (SnO_2) with tetragonal structure in the purple surfaces.

These results correspond to the recipes in found in the Sureda's notebook [11]. A basic flux is described, bearing 4 ounces of lead oxide, 1 ounce of silica and, optionally, borax, "*suitable for all colors*". The use of a unique flux allowed to formulate all required colors with different pigment mixtures and to optimize the firing temperature. The over-glaze painting technique and the colors preparation was similar to employed in other European porcelains in the eighteen century [14] and, with some exceptions like Cassius purple, the same that was traditionally employed in maiolica productions [15].

4. The firing process and the interfaces

Decorated porcelain was fired at least three times. After an initial firing at low temperature, it is produced a hardly sintered porcelain, named biscuit, over which the glaze is easily applied. Then, in a second firing at high temperature, porcelain densifies, glaze vitrifies and the body/glaze interface is formed. This is a hard interface as the vitreous phase composition in the body is similar to the feldspathic glaze. Paste and glaze compositions must be adjusted to match as possible their dilatation coefficients. If not, cracking or crazing is produced during cooling and in the next firing.

In the third firing, painted enamels are fixed to the glaze surface at low temperature, usually lower than 900 ºC if considered the PbO content and the stability of crystalline pigments. Mismatch between the soft lead-silica enamels and the hard feldspathic glaze causes a weak interface where small cracks can appear during cooling (Image 3).

5. Tiles degradation

Tiles must be considered as a layered composite system, of both materials and interfaces. The degradation or the durability of the whole will be conditioned by the most alterable of components.

Consequently, the most evident pathology of the two porcelain floors of Aranjuez is the near complete and irreversible loss of painted decoration. The high concentration of fluxes, lead oxide or borax, in the color layer and the low temperature and short firing treatment make especially weaker the enamel and the enamel/glaze interface.

In this case, main wear mechanism is obviously the abrasion due to the inevitable foot traffic as visitors, although very limited, must necessarily go through the two rooms. A carpet protects floors in the restrict traffic areas.

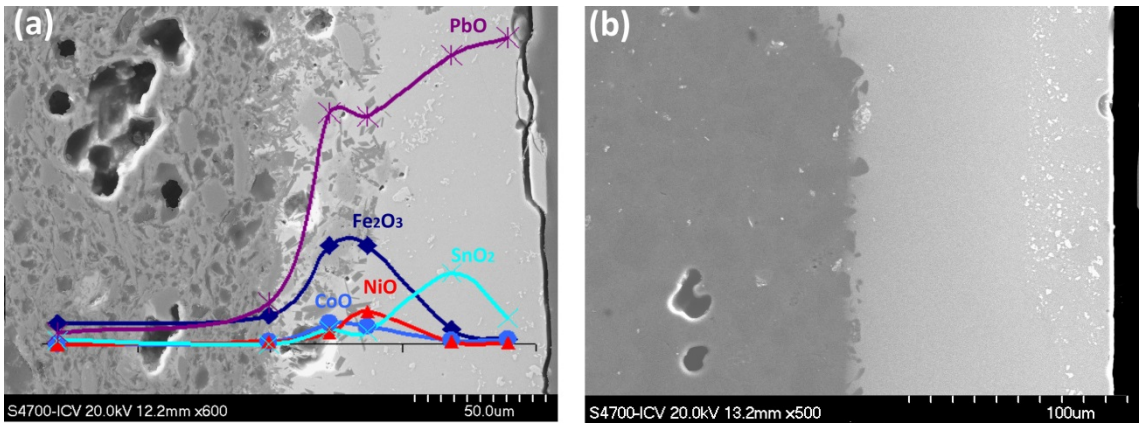

Image 4. (a). Scheme of concentration at the body/ glaze interface of a under-glaze colored maiolica (b) Naples yellow particles crystallized inside the lead-alkali glaze of a soft porcelain.

Ceramic characterization can resolve two more questions: why porcelain floors were done; and why the Aranjuez tiles are much more decolored than historic maiolica flooring tiles.

There were many reasons to fabricate the porcelain floors. Besides the luxury hobbies of the king, the first reason was the use of sepiolite as raw material; pavements needed tons of porcelain to be fabricated and local sepiolite was considerably cheaper than the Spanish kaolin. Second reason was the low porosity of porcelain if compared with earthenware and higher hardness of feldspathic glazes if compared with lead-alkali or tin-lead-alkali glazes.

Other reason was that Buen Retiro continued in Aranjuez the historic tradition of polychrome ceramics floors that started in Spain during the Nazarí kingdom in the twelfth century and that persisted in the Southern Europe at the beginning of the nineteenth century.

Maiolica earthen body consisting of an open network of quartz and reacting clay relicts scarcely vitrified, Image 4-a. Co blue pigment was painted on the body surface (under-glaze) and then cover with the tin-lead-alkali glace. Figure 4-b shows soft porcelain with a highly dense and vitrified body covered with a lead-alkali glaze. Naples yellow was over-glaze painted on, but pigments particles are diffused into, and then protect by the soft glace. Painting soft colors over hard feldspathic glaze was not a good option of ceramics floors, although glazes and bodies were are notably well conserved.

Flooring porcelain tiles of Aranjuez, despite the loss of color, should be care as outstanding good of the Cultural and Historical Heritage.

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